

CO₂ CAPTURE FROM GASES USING ACTIVATED CARBON

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In Partial Fulfillment of the Requirements
For the Degree of Doctor of Philosophy
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Abstract

Research on the CO₂ adsorption on activated carbon (AC) adsorbents has gained significant interest due to their low cost, low regeneration energy, and eco-friendly characteristics. The current research was focused on the systematic development of AC using different types of biomass, pyrolysis conditions and activation conditions to prepare adsorbent with tailored textural properties for CO₂ separation under simulated flue gas conditions. Impact of MgO impregnation on CO₂ adsorption behavior of AC was also studied and an isothermal mass transfer model was developed to model the CO₂ adsorption process in a binary mixture on porous carbon. The work was divided into four phases. The first phase of the work was focused on the synthesis of activated carbon using steam, CO₂ and potassium hydroxide (KOH) as activating agents and evaluation of the CO₂ adsorption performance under a range of temperature and inlet CO₂ concentrations (C_{CO_2}). The KOH treated activated carbon had the best CO₂ adsorption performance of 1.8 mol/kg due to its microporous structure under the optimized experimental conditions of 30 mol% CO₂ and 25°C. All prepared activated carbon samples had a better performance at low temperature (~25°C) and/or high C_{CO_2} (~30 mol%). In the second phase, the KOH activation conditions in the first phase was used for the activated carbon preparation using three different types of biomass (forest residue, agricultural residue and animal manure) as precursor and two different pyrolysis processes (fast and slow pyrolysis). The main finding in this phase was that activated carbons have different sensitivity to CO₂ separation according to their micro-pore distributions; and total pore volume and surface area are not significant factors for CO₂ adsorption on ACs. Overall, the pinewood saw dust derived ACs showed the best adsorption capacity of 78.1 mg/g (at 15 mol% CO₂ in N₂ and 25°C). In phase 3, the results of impregnating AC with magnesium oxide (MgO) showed that preparation method has a greater impact than metal content on the surface area and porosity of ACs. Moreover, MgO impregnation of AC overcomes the limitation of using not-impregnated AC at moderate temperature and low partial pressure of CO₂. In the phase 4, an isothermal mass transfer model for CO₂ adsorption in a mixture of CO₂/N₂ has been developed. The adsorption equilibrium data of CO₂ on KOH activated carbon were determined at 273, 298, 323 and 348 K. The simulation of CO₂ adsorption in a fixed-bed of activated carbon was performed in Python using a bi-Linear Driving Force (bi-LDF) approximation for isothermal mass transfer. The model was used to

reproduce the CO₂ adsorption breakthrough curves for CO₂/N₂ gas mixture and it can be used for designing a fixed-bed adsorption process to separate CO₂ and N₂ using microporous and mesoporous carbon materials.

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Nomenclature

- b_{0i} = temperature - independent constant of Langmuir isotherm of component i, kPa^{-1}
 b_{ij} = constant of Langmuir isotherm of component i, kPa^{-1}
 c_i = concentration of component i in bulk gas phase, mol/m^3
 c_{pi} = concentration of component i in macropores, mol/m^3
 $\overline{c_{pi}}$ = average concentration of component i in macropores, mol/m^3
 C = total concentration of bulk gas phase, mol/m^3
 C_{CO_2} = CO_2 content
 d_p = particle diameter, m
 $D_{\text{ax},i}$ = axial dispersion of component i, m^2/s
 D_{ci} = crystal diffusivity of component i, m^2/s
 D_{ci0} = temperature - independent pre - exponential constant of component i, m^2/s
 D_{ci}^∞ = temperature dependant diffusivity constant of component i, m^2/s
 $D_{i,j}^\infty$ = binary molecular diffusion coefficient at a reference temperature and pressure, m^2/s
 $D_{i,j}$ = binary molecular diffusion coefficient, m^2/s
 $D_{K,i}$ = Knudsen diffusivity of component i, m^2/s
 $D_{m,i}$ = molecular diffusivity of component i, m^2/s
 D_{pi} = effective macropore diffusivity of component i, m^2/s
 $E_{a,i}$ = diffusion activation energy of component i, J/mol
 H = Henry's law constant
 ΔH_i = adsorption heat of component i, J/mol
 k_{fi} = particle - to - fluid mass transfer coefficient
 n : the number of independent process variables
 n_c : the number of center points or replicates
 q_{ci}^* = equilibrium adsorbed concentration of component i, mol/kg
 q_{si} = saturation capacity of component i, mol/g
 $\overline{q_{ci}}$ = average adsorbed concentration of component i per unit of particle volume, mol/kg
 $\overline{q_{pi}}$ = average adsorbed concentration of component i per unit of adsorbent bed volume, mol/kg
 r_c = radius of crystal, m
 r_p = pore radius, m
 R = universal gas constant, J/Kmol

R = universal gas constant, J/Kmol

R_p = Particle radius, m

t = time, s

T = temperature, K

t_b = breakthrough time, °C

u = gas velocity, m/s

$V_{p,b}$ = pore volume determined from CO_2 and N_2 adsorption data at 298 K and 77 K, m^3/kg

V_c = volume of packed - bed, m^3

W = weight of powder, kg

X , Y , and Z = regression coefficients for chemical compound

y_i = mole fraction of component i

Greek Symbols

ε_b = bed porosity

ε_p = particle porosity

ε_t = total porosity

η_f = viscosity of gas mixture, kg/m.s(Pa.s)

η_i = viscosity of component i , kg/m.s(Pa.s)

λ_p = Equivalent spherical diameter of the particle

ρ_f = density of gas stream, kg/m^3

ρ_i = density of component i , kg/m^3

ρ_s = absolute or skeletal density, kg/m^3

ρ_p = particle density

τ_k = Knudsen tortuosity factor

τ = tortuosity factor

$\phi_{i,j}$ = Wilke's parameter

Abbreviations

3MgO-AC: 3 wt. % MgO loaded activated carbon

3MgO-AC-R: 3 wt. % MgO loaded activated carbon-rinsed

3MgO-AC-DRY: 3 wt. % MgO incipient impregnated activated carbon

3MgO-B: 3 wt. % MgO loaded biochar

3MgO-B-R: 3 wt. % MgO loaded biochar-rinsed

10MgO-AC: 10 wt. % MgO loaded activated carbon

10MgO-AC-R: 10 wt. % MgO loaded activated carbon-rinsed

10MgO-AC-DRY: 10 wt. % MgO incipient impregnated activated carbon

10MgO-B: 10 wt. % MgO loaded biochar

10MgO-B-R: 10 wt. % MgO loaded biochar-rinsed

AC: activated carbons

ANOVA: Analysis of Variance

BET: Brunauer, Emmett, and Teller

Bi-LDF: Bi-linear Driving Force

CCD: Central Composite Design

df: degree of freedom

DFT: density Functional Theory

FP: fast pyrolysis

FS: flax straw

FTIR: Fourier Transform Infra-Red,

FWHM: full width at half maximum

GAI: Generalized Adsorption Isotherm

GC: Gas Chromatograph

H₃PO₄: phosphoric acid

He: helium

IPCC: The Intergovernmental Panel on Climate Change

IUPAC: International Union of Pure and Applied Chemistry

KOH: potassium hydroxide

LDF: Linear Driving Force

MFC: Mass Flow Controller

MgCl₂: Magnesium chloride
Mg (NO₃)₂·6H₂O: Magnesium nitrate hexahydrate
MgO: magnesium oxide
MTZ: Mass Transfer Zone
NaOH: sodium hydroxide
NEXAFS: Near Edge X-ray Absorption Fine Structure
NLDFT: Non-Local Density Functional Theory
PL: poultry litter
PSD: Particle Size Distribution
REIXS: The Resonant Elastic and Inelastic X-ray Scattering
SD: saw dust
SEM: Scanning Electron Microscope
SGM: spherical grating monochromator
SP: slow pyrolysis
TCD: Thermal Conductivity Detector
TGA: ThermoGravimetric Analyzer
TPD: Temperature-Programmed Desorption
TSA: Temperature Swing Adsorption
WR: willow ring
WS: wheat straw
XPS: X-Ray Photoelectron Spectroscopy
XRD: X-Ray Diffraction

Chapter 1 Introduction and Thesis Outline

1.1 Introduction

Global warming has become one of the most important environmental problems in 21st century¹ and the rise in CO₂ emissions is considered as the main cause for the global warming. The highest rise in average temperature was observed in the 30-year period of 1983 to 2012 of the last 1400 years in the northern hemisphere² which results in 0.85 °C global surface temperature increase in the period of 1880-2012². After Kyoto protocol came into force in 2005 more attention is devoted to this matter. However, signatories of the Kyoto protocol didn't meet their commitments to decrease emissions and the CO₂ content level in atmosphere is recorded to be 400.40 ppm in November 2015³. The mitigation scenarios include “energy efficiency optimization, zero and low carbon energy supplies including nuclear power, fossil fuel energies with carbon dioxide capture and storage units, renewable energy sources, enhancement of biological sinks, and reduction of non- CO₂ greenhouse gas emissions”⁴. In the absence of mitigation policies, if CO₂ emission increases with the same rate, it is estimated that CO₂ concentrations in the atmosphere could increase to 600–1550 ppm in 2030⁵. It corresponds to 4.1°C – 4.8°C above pre-industrial average global temperature by the end of the 21st century. Carbon capture from major CO₂ emitting industries like coal-fired power plants and fossil-fuel based plants is one of the immediate options to address this issue. In the 11th session of the Conference of the Parties serving as the meeting of the Parties to the Kyoto Protocol (CMP 11)⁶ that took place from 30 November to 11 December 2015 in Paris, the members agreed to limit average global temperature over the 21st century to below 2°C above the pre-industrial levels⁶. However, in most of discussed scenarios, fossil fuel is the main source of energy at least until 2050. So, carbon capture and sequestration could be a main option to address this problem and facilitate stabilizing the atmospheric CO₂ concentrations.

Depending on the fuel type, CO₂ partial pressure and gas stream pressure, three types of carbon capture techniques can be used: post-combustion, pre-combustion and oxyfuel combustion. The schematic of these processes are shown in Figure 1-1⁵. Pre-combustion capture processes convert fuel into a mixture of hydrogen and CO₂. The separated hydrogen can be burnt with zero-emission of CO₂. Post-combustion processes separate CO₂ from combustion flue gas stream. In

oxyfuel capture processes, pure oxygen is used for fuel combustion. The exhaust gases of this process are water vapor and CO_2 .

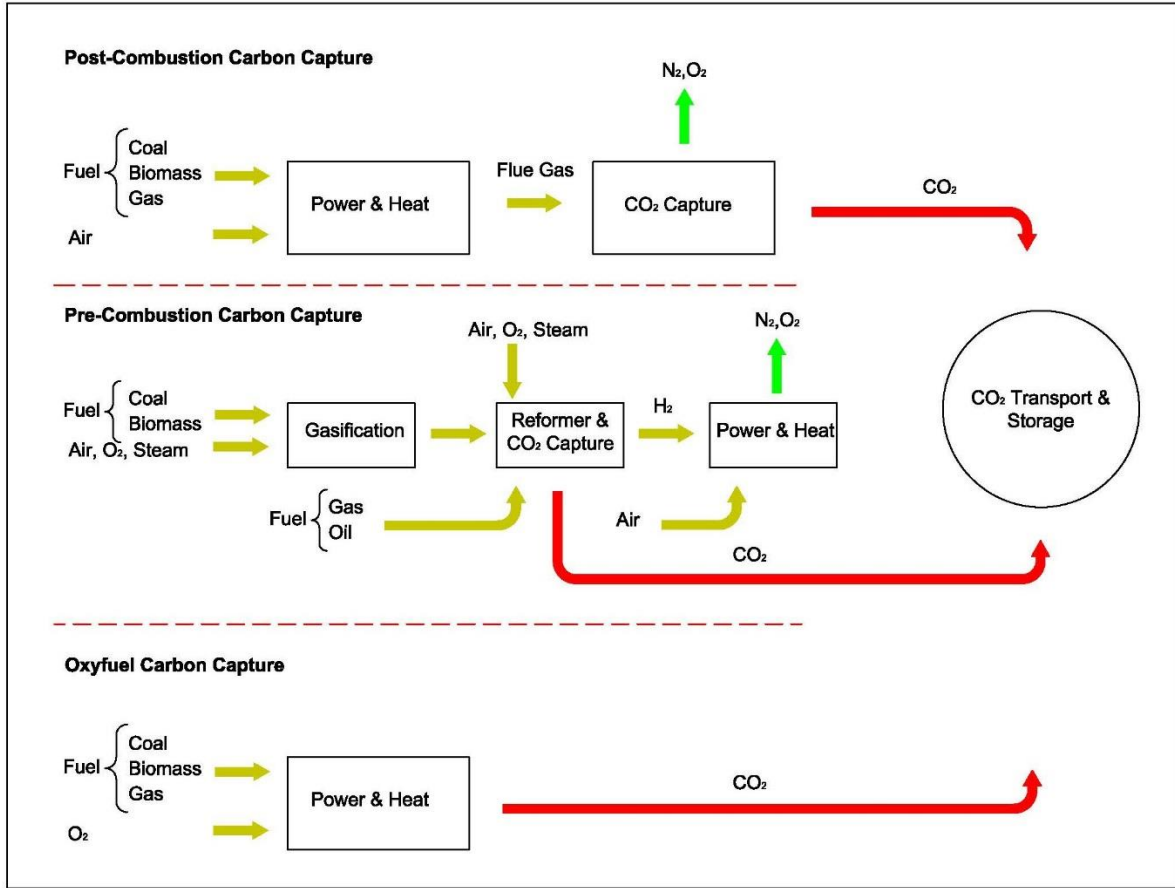


Figure 1-1: Schematic representation of post-combustion, pre-combustion and oxyfuel combustion

Post combustion carbon capture is the preferred technique to reduce CO_2 emission from the existing power plants⁵. All the commercially available processes are similar in concept. Figure 1-2 shows the schematic of this process⁴. The low concentration of CO_2 means that a huge amount of gas should be treated at a high capital cost. The energy penalty associated with the stripping of CO_2 and regeneration of solvent is one of the main technology challenges that must be overcome for the amine absorption based technology in power plants. Two other concerns with amine

solvents are corrosion problem, in the presence of oxygen, and high solvent degradation rates^{5,7-9}.

Due to this operation problems involved in amine absorption process, alternative methods are considered. One of these alternatives is CO₂ adsorption on solid surfaces. Due to the large volume to flue gas, capital cost of post-combustion process is large. So, using expensive sorbent materials or material with high disposal expenses can escalate cost related to the process and make it economically unfeasible⁴. Based on IPCC report¹⁰, a selective adsorbent with high CO₂ uptake might make the design of a full-scale adsorption unit feasible¹¹. The ideal adsorbent for CO₂ separation should have some important characteristics such as: high CO₂ adsorption capacity, appropriate selectivity over N₂ and CH₄ and high stability in repetitive cyclic adsorption/desorption process⁵. This thesis focuses on development of low-cost and effective adsorbents for CO₂ capture from coal-fired power plants.

Based on the literature review discussion in chapter 2 the following knowledge gaps were identified:

- Study of impacts of precursor, pyrolysis conditions and activating agents on porosity, surface chemistry of activated carbon were missing from literature.
- The adsorption of CO₂, in competition with N₂ and other flue gas components were mostly discussed in terms of surface area and surface chemistry. Contribution of parameters such as total pore volume, micro pore volume and ultra micropore on CO₂ adsorption of activated carbon is not clearly understood
- Most of results in the literature are reported based on equilibrium adsorption of CO₂ using pure CO₂ or mixed with an inert gas. Measurement of CO₂ adsorption on activated carbon at low partial pressure of CO₂ (5-15 mol. %) and moderate temperature is very limited.
- Research work on performance study of activated under simulated flue gas conditions require attention. study of the solid adsorbents using simulated post combustion flue gas and different bed configuration can enhance adsorption/desorption performance for CO₂ separation

- Several amine-impregnated solid sorbents were developed using various amine groups to enhance CO₂ adsorption. However, the potential application of impregnation of activated carbon with metal oxides to improve CO₂ adsorption performance at low and moderate temperature in comparison with other surface treatment didn't discussed in the literature.
- Mathematical modeling of the fixed-bed adsorption of carbon dioxide using different mass transfer mechanisms have been discussed in the literature. However, limited work is reported on adsorption kinetics of CO₂/N₂ adsorption on activated carbons for post combustion conditions.

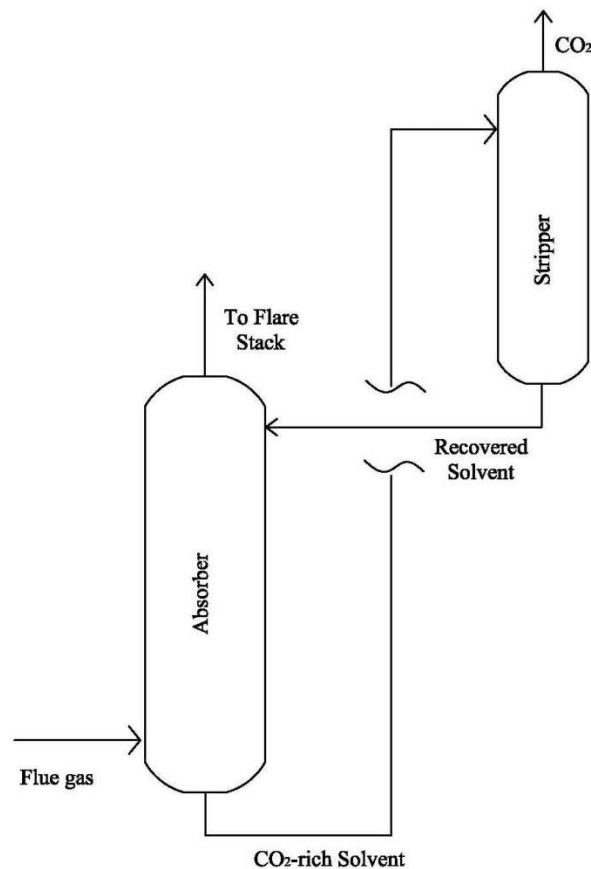


Figure 1-2: Schematic of an amine-based CO₂ capture system

1.2 Objective:

The abundance of biomass precursors in Saskatchewan, their important role in the Canadian economy, and the increasing demand and market for environmental applications of biochar and

activated carbon are the motivation for this research project. The underlying principle behind my research was to carbonize the waste biomass in Saskatchewan, convert it to activated carbons as a value added product and use this activated carbon for separation of carbon dioxide from coal-fired power plants. Since the impact of precursors, carbonization method, activating agents and conditions, metal impregnation on physical and chemical properties and CO₂ adsorption behavior of activated carbon are not clear, the following objectives and sub-objectives were set in this work:

- Preparation of activated carbon using three different activating agents:
 - Synthesis of activated carbons from a low cost source in Canada using different activating agents: physical activation (steam and CO₂) and chemical activation (KOH) and their characterizations.
 - Characterization of the produced activated carbons.
 - Evaluation of the impact of activating agents on CO₂ adsorption performance of the produced activated carbons using various flue gas mixture (10-30 mol. % of CO₂ in He) at 25-65 °C and atmospheric pressure.
- Preparation of activated carbon from different Canadian waste biomasses under different carbonization conditions:
 - Preparation of activated carbons from different sources of biomass and different carbonization techniques: the forest residues (willow ring and saw dust), the agricultural residues (wheat straw and flax Straw) and the animal manure (poultry litter)
 - Characterization of the produced activated carbons.
 - Evaluation of the impact of precursors and pyrolysis methods on CO₂ adsorption capacity, selectivity and stability of produced activated carbons under the flue gas mixture of 15 mol. % of CO₂, 5 mol. % of O₂ and 80% of N₂ at 25 °C and atmospheric pressure.
- Preparation of metal impregnated activated carbons using different impregnation technique and metal content:

- Preparation of metal impregnated mesoporous activated carbon using: excess solution impregnation of activated carbon, incipient wetness impregnation of activated carbon and excess solution impregnation of biochar.
- Evaluation of impacts of washing step and metal content on porosity and surface chemistry of activated carbon.
- Evaluation of performance of metal impregnated carbons for CO₂ adsorption at 25 and 100 °C in a gas mixture of 15wt. % CO₂ in N₂.
- Development of a reliable isothermal mass transfer model to simulate CO₂ adsorption
 - Fit a full set of equilibrium data with Langmuir adsorption model.
 - Development of an isothermal mass transfer model to express the performance of the fixed-bed adsorption column for CO₂ adsorption in a binary mixture of CO₂/N₂ in the range of post-combustion operation conditions.
 - Validation of the model with experimental data.

1.3 Thesis outline

Chapter 2 of this thesis is devoted to a comprehensive literature review of post combustion CO₂ capture, CO₂ adsorption, adsorption isotherms, surface area and porosity, synthesis of activated carbons and their properties for CO₂ separation and mass transfer parameters and models for gas adsorption on activated carbons.

To study the effects of activating agents on physical and chemical properties of the activated carbons, activated carbons are prepared from biochar (by product of fast pyrolysis of Whitewood) using three different activating agents of steam, CO₂ and potassium hydroxide using a fixed- bed reactor. In chapter 3, the details of activation methods and conditions, textural properties and surface chemistry of the activated carbons, and CO₂ adsorption capacity and stability of these adsorbents in a binary mixture of CO₂/ He at atmospheric pressure, temperature range of 25-65 °C and inlet CO₂ concentrations range of 10-30 mol. % are discussed.

It is known that the heteroatoms, derived from precursors, become a part of chemical structure during the carbonization. Biochars derived from different sources and carbonization techniques have different physical and chemical properties¹². Therefore, preparation of activated carbons

from different precursors or carbonization conditions affects adsorption characteristics of these adsorbents. In chapter 4, the effects of precursors and pyrolysis methods on textural properties and surface functional groups of activated carbons are evaluated. Activated carbons are produced from different waste biomasses including agricultural waste (wheat straw and flax straw), forest residue (saw dust and willow ring) and animal manure (poultry litter). The precursors are carbonized through the fast and slow pyrolysis processes and then activated with potassium hydroxide. The adsorption capacity, selectivity and stability of the produced activated carbon is measured under a flue gas condition of 15 mol% of CO₂, 5 mol% of O₂ and 80% of N₂ at 25 °C and atmospheric pressure.

More importantly, surface properties of activated carbons can be modified by metal oxide impregnation^{13,14}. Magnesium oxide (MgO) is available in natural minerals and can be produced at low cost^{15,16}. Selective CO₂ chemisorption on MgO at moderate temperature levels is reported in the literature, indicating that it needs a lower regeneration energy compared to other metal oxides¹⁵. In chapter 5, the effects of impregnation methods and metal content (3 and 10 wt. %) on adsorption capacity and stability of activated carbons are evaluated. Steam activated carbons are impregnated with MgO using two methods of incipient wetness and excess solution impregnation process. CO₂ Adsorption properties of these adsorbents are compared to single-step prepared activated carbons. In this method, biochar is impregnated with MgO followed by steam activation and the products are compared in terms of porosity, surface chemistry and CO₂ adsorption capacity from a feed mixture of 15% CO₂ in N₂ in a fixed-bed reactor.

A kinetic study is the last step in developing a low-cost adsorbent with tailored adsorptive properties for CO₂. Chapter 6 includes an isothermal bi-LDF model for adsorption in a fixed-bed reactor to confirm the experimental results in this thesis. The details of mass transfer effects on activated carbons and adsorption process are examined.

Chapter 7 summarizes all the findings of Chapters 3-6 and provides some recommendations for possible future works.

Chapter 2 Literature Review

This chapter provides a review of the post combustion CO₂ capture, breakthrough CO₂ adsorption, adsorption isotherms, surface area and porosity measurements, proper adsorbents for this process, synthesis of activated carbon, its porous structure and surface chemistry, and mass balance in packed-bed reactor and related mass transfer parameters for gas adsorption.

2.1 Carbon dioxide chemistry

Carbon dioxide (CO₂) is a non-polar, colorless and odorless gas composed of a carbon atom double bonded to two oxygen atoms. CO₂ has sixteen bonding electrons in its valence shell. The C=O bonds are equivalent and are short (1.16 °A), and the molecular diameter is 3.30 °A¹⁷. Although both carbon-oxygen bonds are polar, the CO₂ molecule doesn't have a permanent electrical dipole due to its centrosymmetric structure. Since two equal dipoles are located nearby, their total dipole moment is zero. Therefore, “only two vibrational bands are detected in the IR spectrum¹⁸ : antisymmetric stretching mode at 2350 cm⁻¹ and a degenerate pair of bending modes at 667 cm⁻¹”¹⁸. However, CO₂ molecule has a strong quadrupole (-13.71E-40 Coulomb/m²) as their positive charges overlap¹⁹. This quadrupole interacts with the carbon lattice, allowing the gas molecule to enter the pores. Other flue gas component such as nitrogen, hydrogen, oxygen and methane have much smaller quadrupole moments which facilitate CO₂ interaction with walls inside activated carbon pores in competition with other component²⁰. Physical properties of CO₂ is provided in Table 2-1^{21,22}:

Table 2-1: Physical properties of CO₂

Molecular weight (g/mol)	44.01
Critical temperature (°C)	31.1
Critical pressure (bar)	73.9 bar
Boiling point @1.013 bar (°C)	- 78.5
Specific volume @ STP	0.506 m ³ kg ⁻¹
Gas density @ STP	1.976 kg m ⁻³
Viscosity @ STP	13.72 μN.s m ⁻²
PH of saturated CO ₂ solutions	3.7

2.2 Post combustion carbon capture

CO₂ removal from a flue gas stream is referred to as post-combustion CO₂ capture. Post-combustion CO₂ capture is followed by compression, transportation and storage of CO₂²³.

Around 25% of world energy supplies are provided by coal as the world's most abundant fossil fuel source²⁴. On the other hand, more than two third of coal-fired power plants are less than 10 years old²⁵ which makes post combustion carbon capture a vital unit to avoid more CO₂ emission to the atmosphere. A typical flue gas properties of a coal-fired power plant is shown in Table 2-2^{19,26,27}.

Table 2-2: Properties of flue gas streams from coal-fired power plants

Species	Concentration	Kinetic Diameter	Dipole moment	Quadrupole moment	Polarizability
	(vol. %)	(nm)	Debye	10 ⁻⁴⁰ Coulomb·m ²	(10 ⁻²⁴ cm ³)
CO ₂	15-16%	0.330	0	-13.71, -10.00	2.64,2.91,3.02
O ₂	3-4%	0.346	0	-1.33	1.57, 1.77
H ₂ O	5-7	0.280	1.85	-6.67	1.45,1.48
N ₂	Balance	0.364	0	-4.91	0.78, 1.74
SO ₂	800 ppm	0.360	1.63	-14.6	3.72,3.89,4.28
NO	150 ppm	0.317	0.16	-6.00	1.7
NO ₂		0.340	0.316	unknown	3.02
N ₂ O		0.317	0.16,0.54	-12.02, 10.00	3.03, 3.32
HCL	100 ppm	0.346	1.11,3.57	13.28	2.63,2.94
CO	20 ppm	0.376	0.11, 0.37	-8.33, -6.92	1.95,2.19
Ar	~1%	0.340	0	0	1.64,1.83
CH ₄	10 ppm	0.380	0	0	2.6
Flue Gas Process Conditions					
Temperature	25-180	°C			

2.3 CO₂ adsorption

In an adsorption process, a gas mixture contacts a solid surface which can physically or chemically adsorb a component and remove it from the gas mixture. Adsorption is effective in dilute gas mixture¹⁹. Adsorptive is the component in the gas mixture before adsorption. It is referred to adsorbate when it adheres to the solid surface or adsorbent¹⁹. Depending on the nature of the surface forces; there are two different types of adsorption: physical adsorption and chemisorption. In physical adsorption, the Van der Waals forces are dominant while in chemisorption, a chemical bond is formed which is much stronger than Van der Waals forces.

Gas separation in a gas mixture is resulted from one or some of the following: 1) molecular size and/or shape of gas component, 2) the different diffusion rates, 3) the thermodynamic effect (based on the pore wall- gas interactions), and 4) the quantum effect and different diffusion rates in the narrow micropores²⁸. With nonpolar adsorbents like activated carbon, the Van der Waals forces are dominant, and the size and polarizability of adsorbate, and pore size distribution of adsorbent are the main factors while surface chemistry of the adsorbent is less dominant²⁹. As mentioned above, a large specific surface area is preferable and pore size distribution affects the accessibility or selectivity of the adsorbate to the adsorbent. The pore size classification is assigned by the International Union of Pure and Applied Chemistry (IUPAC)^{19,30} and is shown in Table 2-3.

Table 2-3: IUPAC classification of pore sizes

Type	Pore size (nm)
Ultramicro-pores	<0.7
Supermicro-pore	0.7-2
Micro-pore	<2
Meso-pore	2-50
Macro-pore	>50

2.3.1 Adsorption dynamics, breakthrough curves and selectivity

A fixed-bed is used on a continuous basis till saturation and then it is disposed of or regenerated for multiple usages. The performance of fixed-beds is evaluated using a breakthrough curve. A

breakthrough curve expresses the increase in the ratio of outlet concentration to the inlet concentration (C_{out}/C_{in}) versus time¹⁹. At a constant inlet gas concentration, the S – shaped breakthrough curve shows the increase in gas content at outlet from zero to one¹⁹. Figure 2-2 shows the schematic of an adsorption breakthrough curve. The three zones are shown within the bed: (1) the saturated zone nearest the inlet which is in equilibrium with the CO₂ feed concentration, (2) adsorption zone with S-shape curve, and (3) a fresh zone in which no adsorption takes place¹⁹.

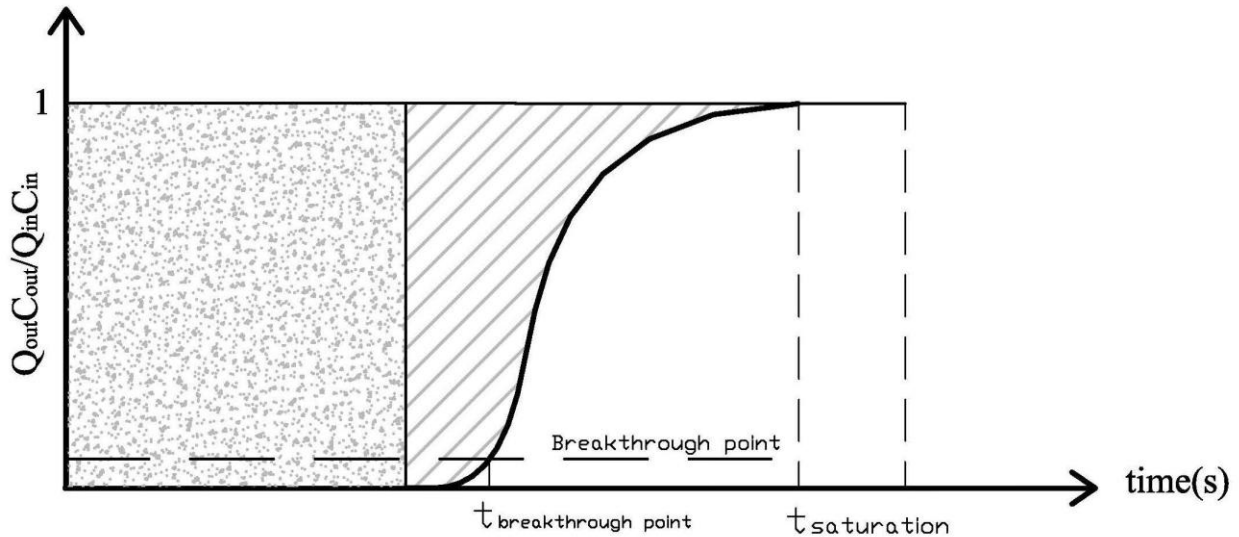


Figure 2-2: Typical breakthrough curve

The breakthrough point is the point in the breakthrough curve at which the outlet concentration reaches a predetermined value. This point depends on the effluent composition. For CO₂ separation, the breakthrough point is usually below 5% of the inlet concentration. The breakthrough time and the slope of the curve are important characteristics of the fixed-bed separation. The fixed-bed adsorption occurs layer by layer over a portion of the bed called mass transfer zone (MTZ) during the operation time. Mass transfer zone starts moving along the bed, from the inlet to the outlet point. Within the MTZ, the degree of saturation with adsorbate decreases from 100% to zero. When this zone is saturated, the MTZ will travel through the bed and a fresh section of bed is in front of the leading edge of the MTZ. When a greater portion of the bed is saturated, the breakthrough point occurs (Figure 2-3). An optimal sorbent has a narrow mass-transfer zone which makes the most efficient use of the sorbent. In fact, a vertical

breakthrough curve and zero mass-transfer resistance and minimal axial dispersion represent an ideal adsorption process.

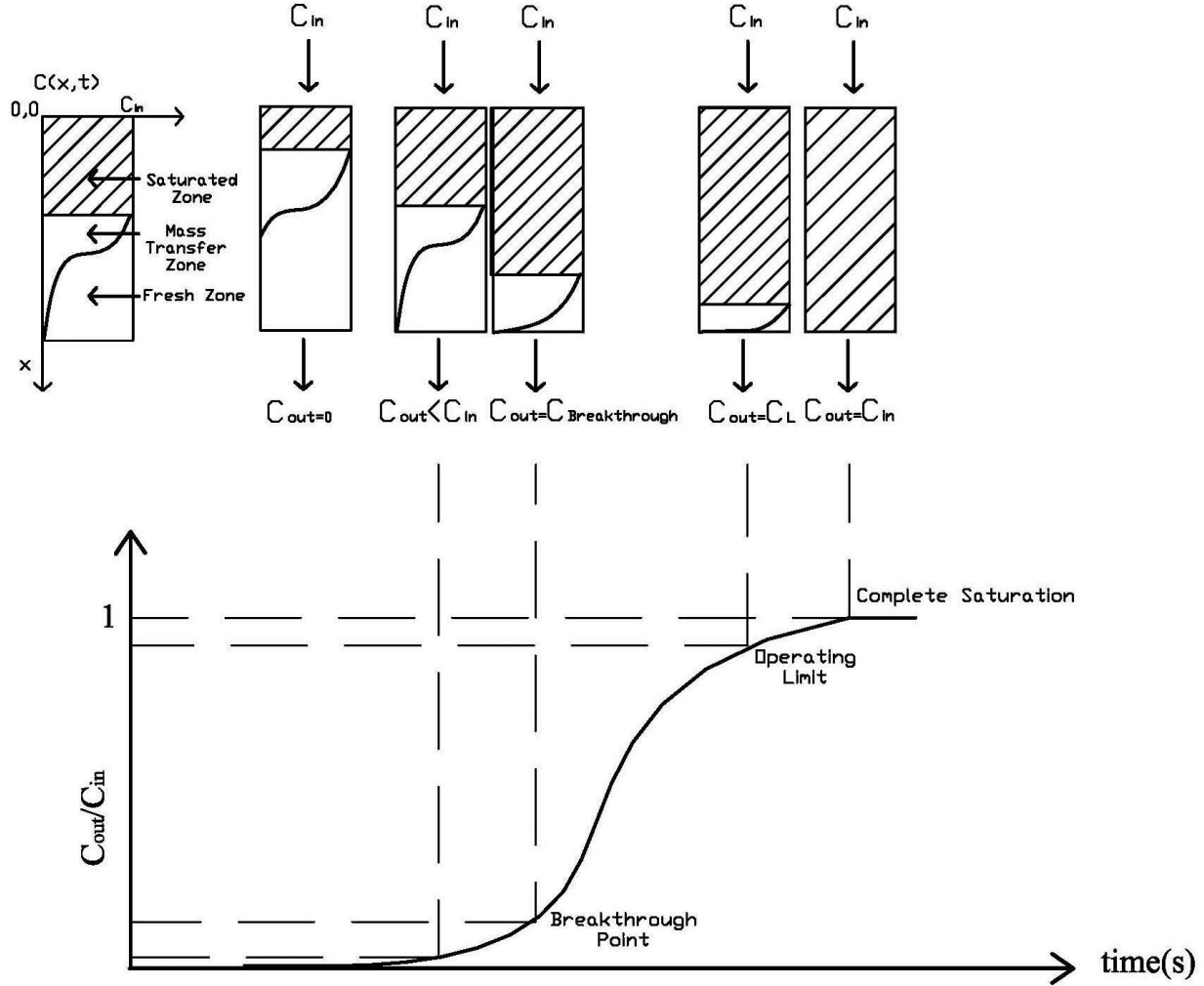


Figure 2-3: Travel of Mass transfer zone through the bed and the corresponding breakthrough curve

The amount of gas adsorbed on adsorbents (S , mol/g) at a certain time (t , s) at a constant temperature and inlet gas concentration can be determined by applying Eqs. 2-1 to 2-4^{31,32}:

$$S = \frac{M_{\text{adsorbate}}}{m_{\text{Adsorbent}}} \left[\overbrace{\int_0^{t_s} (Q_{\text{in}} C_{\text{in}} - Q_{\text{out}} C_{\text{out}}) dt}^a - \overbrace{\frac{C_{\text{in}} P \epsilon_T V_c}{ZRT}}^b \right] \quad (2-1)$$

$$\varepsilon_T = \varepsilon_b + (1 - \varepsilon_b)\varepsilon_p \quad (2-2)$$

$$\varepsilon_b = 1 - \frac{W/V_c}{\rho_p} \quad (2-3)$$

$$\varepsilon_p = 1 - \frac{\rho_p}{\rho_s} \quad (2-4)$$

where

C_{in} : adsorbate concentration in inlet flow gas, mol. %

C_{out} : adsorbate concentration in outlet flow gas, mol. %

$M_{adsorbate}$: molecular weight of adsorbate

P : pressure, Pa

Q_{in} : inlet flow rate, mole/s

Q_{out} : outlet flow rate, mole/s

R : Universal gas constant, J/mole.K

T : temperature, K

t_s : saturation time, s

V_C : volume of the packed bed, cm^3

W : weight of the sample, g

ε_b : bed porosity

ε_p : particle porosity

ε_T : total bed porosity

ρ_p : particle mercury density, g/cm³

ρ_s : solid density, g/cm³

In Eq. 2-1, the integral term (part a) represent the total mass of CO₂ adsorbed on the adsorbent ($g_{\text{adsorbate}}$) and is calculated by a graphical method (Figure 2-4) using Eqs. 2-5 and 2-6^{32,33}.

$$m = \frac{A_{\text{adsorption}}}{A_{\text{total}}} \times m_{\text{total}} \quad (2-5)$$

$$S_{\text{CO}_2} = \frac{m}{m_{\text{adsorbent}}} \quad (2-6)$$

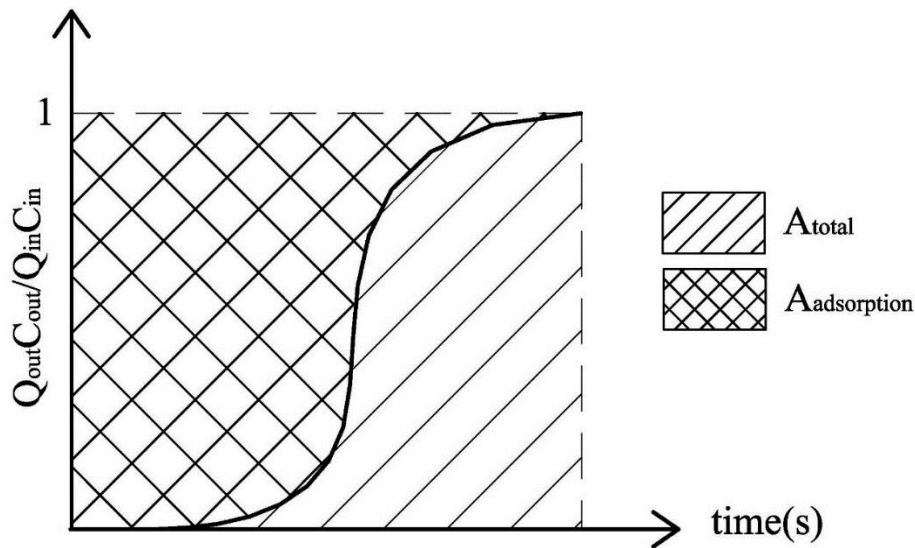


Figure 2-4: Graphical method to calculate the adsorption capacity

where,

A_{total} : total area at saturation time,

$A_{\text{adsorption}}$: area above the curve at time t

m : mass adsorbed at time t , g

$m_{\text{adsorbent}}$: mass of adsorbent bed, g

m_{total} : total mass of CO₂ passing through adsorbent at time t, g

S: capacity of adsorbent bed, $g_{\text{adsorbed}}/g_{\text{adsorbent}}$

A simple method to determine adsorbent selectivity was proposed by Rege and Yang³⁴ based on the equilibrium adsorption capacities. Selectivity of component i over component j in a gas mixture is calculated as follows(Eq. 2-7):³⁴

$$S(i/j) = \frac{x_i/x_j}{y_i/y_j} \quad (2 - 7)$$

where x_i and x_j are the mole fractions of the components of i and j on the adsorbent, and y_i and y_j are the corresponding mole fractions of the components of i and j in the gas mixture.

2.4 Adsorption isotherms

The static adsorption capacity and selectivity of an adsorbent for a single component is usually evaluated using adsorption isotherms, a curve relating the equilibrium concentration of adsorbed phase on the surface as a function of partial pressure of adsorbate in the gas mixture. The six different types of adsorption isotherms are shown in Figure 2-5. Shape of an adsorption isotherm depends on the pore size (mesopore or micropore) and the interaction of the adsorbate with the pore wall. The specific surface area, mean pore size and particle size distribution are calculated using adsorption isotherms¹⁹. Type I or the Langmuir isotherm represents the microporous adsorbents with a single layer or a few molecular layers. Non-porous materials exhibit Type II or Type III (unfavorable) with strong or weak fluid-wall attractive forces, respectively. Types IV and V represent the strong and weak fluid-wall interaction, respectively, in mesoporous structure where capillary condensation occurs. Both Types IV and V types have a hysteresis loops.

Hysteresis loops occur in the multilayer adsorption and associated with capillary condensation. IUPAC classification of hysteresis loops are shown in Figure 2-6^{35,36}. Type H₁ is a fairly narrow loop with very steep and nearly parallel adsorption and desorption branches. Type H₁ loop that represents adsorbents with a narrow distribution of uniform pores has parallel adsorption/desorption branches. Type H₂ loop occurs in the porous materials with pores of different sizes

and shapes. Type H₃ loop usually occurs in the aggregates of porous particles with slit-shaped pores. Hysteresis loop of Type H₄ also occurs by slit-shaped pores but porous materials with dominant microporous structure^{35,36}. Type VI occurs in step-wise adsorption process for some materials with relatively strong fluid-wall forces¹⁹.

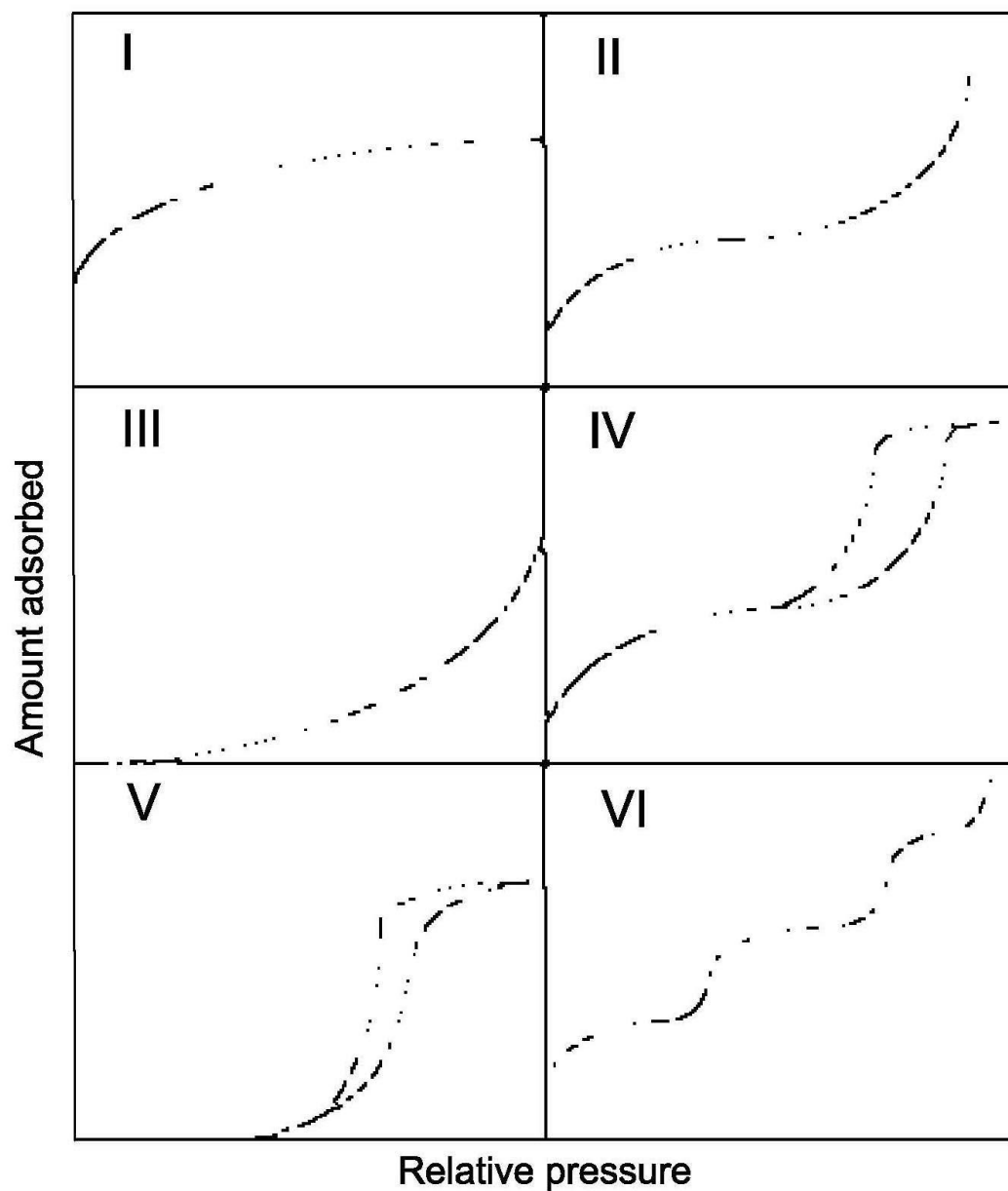


Figure 2-5: IUPAC adsorption Isotherms¹⁹

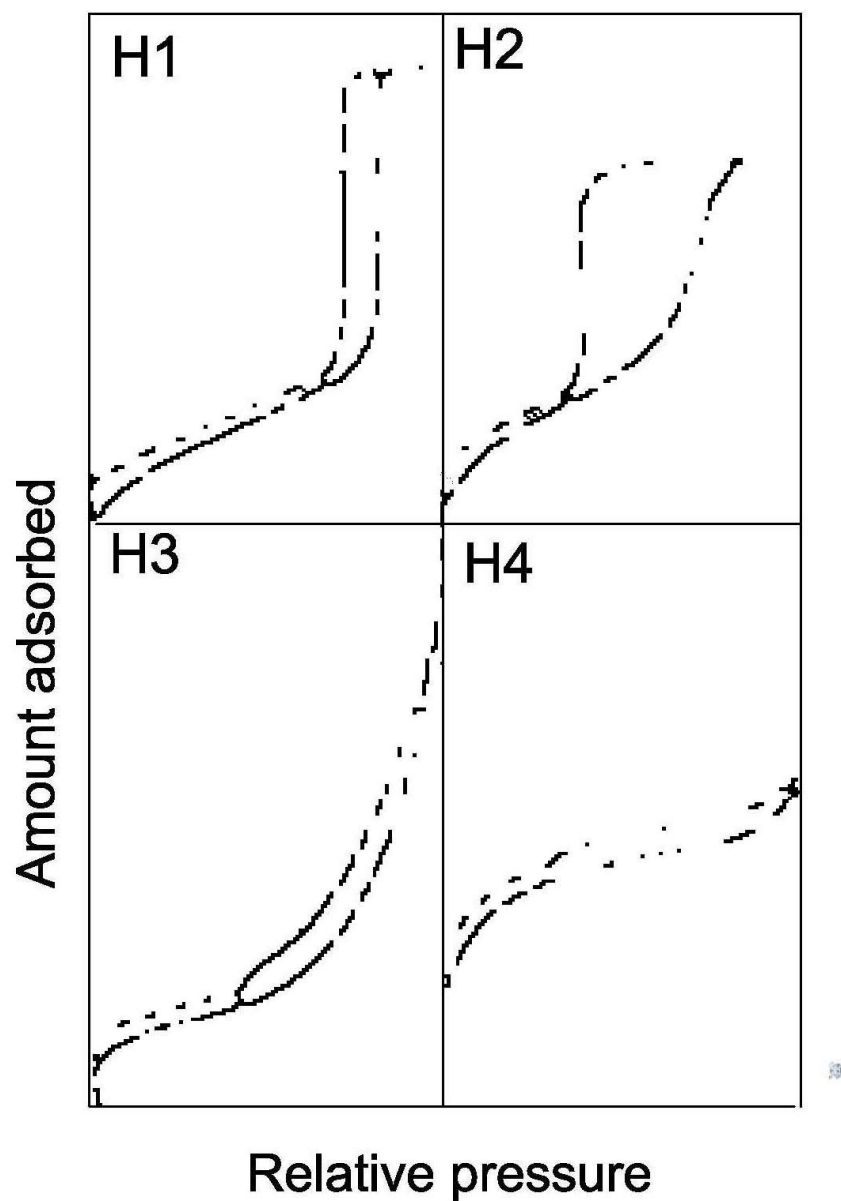


Figure 2-6: Four types of hysteresis loop by IUPAC

2.5 BET surface area and pores size distributions

Nitrogen adsorption at 77K is the standard method for mesopore size analysis. The specific surface area of an adsorbent is determined by N_2 adsorption on solid adsorbent. The Brunauer-

Emmett-Teller (BET) analysis³⁷ is the extended Langmuir adsorption isotherm to multilayer adsorption with the following assumptions:

- 1- a Langmuir isotherm applies to each layer and no transmigration occurs between layers
- 2- All sites on the surface are equivalent
- 3- Multiple nitrogen molecules can be adsorbed to each site
- 4- No interaction between adsorbed molecules exists
- 5- Except for the first layer, nitrogen is in the liquid phase.

The BET equation is shown in Eq. 2-8³⁷:

$$\frac{1}{W((P_0/P) - 1)} = \frac{1}{W_m C} + \frac{C - 1}{W_m C} \left(\frac{P}{P_0} \right) \quad (2 - 8)$$

where

W: weight of gas adsorbed (g)

P/P₀: relative pressure

W_m: weight of adsorbate as monolayer (g)

C: BET constant

Plot of 1/ [W (P₀/P) - 1] vs. P/P₀ yield a linear graph. Using the intercept and slope of this line, the values of W_m and C can be derived.

Total surface area (S_t) and the specific surface area (S_{BET}) are derived as follows (Eq. 2-9 and 2-10):

$$S_t = \frac{W_m N A}{M} \quad (2 - 9)$$

$$S_{BET} = \frac{S_t}{W} \quad (2 - 10)$$

where

N: Avogadro's number (6.023×10^{23})

M: molecular weight of adsorbate

A: adsorbate cross sectional area

The linearity of this plot is limited to a small part of the Type II isotherm ($P/P_0 < 0.1$)³⁸ and at least three data points in this relative pressure range is required.

Total pore volume and pore size distribution

Total pore volume is calculated based on the amount of liquid adsorbed at a relative pressure located after the condensation step³⁹ (usually $P/P_0 = 0.95$) using Eq. 2-11:

$$V_{liq} = \frac{PV_{ads}V_m}{RT} \quad (2-11)$$

where

V_{ads} : volume of adsorbed N_2

V_{liq} : volume of liquid N_2 in pores

V_m : molar volume of liquid adsorbate

P: ambient pressure

T: ambient temperature

Various methods are established to determine the pore size distribution on porous solids. In 1981, Seaton et al.⁴⁰ for the first time suggested using the density functional theory for the pore size distribution of porous carbons from nitrogen adsorption isotherms. In a similar work⁴¹, the porous carbon network was simulated as a continuous size distribution of individual slit-shaped graphitic pores. Considerable progress was made toward our understanding of liquid behavior and its phase changes constrained by the presence of walls, capillaries, and slits in 1980s and this

model is further customized and developed for a full range of porous materials and soon was accepted as a standard method to determine the pore size distribution and analysis of micropores by gas adsorption^{42,43}.

Density functional theory uses the gas-gas and gas-solid interactions to calculate the pore size distribution based on the statistical mechanical model calculations. In this method, a series of isotherms are theoretically developed for the individual pores. The theoretical isotherms that fit the experimental data are selected and the pore size distribution is calculated based on the individual pores.

The relation between theoretical isotherms and the experimental isotherm on a porous solid can be interpreted in terms of a Generalized Adsorption Isotherm (GAI) equation (Eq. 2-12):

$$N(P/P_0) = \int_{W_{min}}^{W_{max}} N(P/P_0, W) f(W) dW \quad (2-12)$$

where

$N(P/P_0)$: experimental adsorption data

W : pore width

$N(P/P_0, W)$: isotherm on a single pore of width W

$f(W)$: pore size distribution function

Typically, grand thermodynamic potential is function of local fluid density, local chemical potential and external potential⁴⁴ (Eq. 2-13).

$$\Omega[\rho(r)] = \underbrace{F[\rho(r)]}_{\text{(fluid-fluid interaction)}} + \int d\rho(r) \left[\underbrace{\phi(r)}_{\text{(solid-fluid interaction)}} - \mu \right] \quad (2-13)$$

where

$F[\rho(r)]$: the free energy functional,

$\phi(r)$: the external potential,

μ : Chemical potential

ρ : local density

The fluid density in the pore is not constant and “it is subjected to adsorption forces in the vicinity of the pore walls”³⁶. “The density distribution can be characterized in terms of a density profile, $\rho(r)$, expressed as a function of distance, r , from the wall across the pore”³⁶. In NLDFT approach, the equilibrium local density profile of the adsorbate for all locations in the pore at a given temperature, chemical potential and volume is calculated by minimization of the grand thermodynamic potential⁴². Once the equilibrium distribution of the fluid local density at a range of the chemical potential is calculated and its averaged fluid local density determined, the theoretical adsorption isotherm can be developed.

Characterization of mesoporous materials is typically determined using N_2 adsorption at 77 K. However, the pore size and volume analysis of the microporous materials with N_2 is not accurate. The saturation pressure of N_2 at 77 K is 760 Torr. The pore filling in ultra-micro pores requires a very low relative pressure (e.g. 10^{-8}) which results in a limited diffusion and very slow adsorption equilibrium which challenges the sensitivity of the N_2 adsorption to determine the pore size distribution of the microporous materials. To overcome the slow diffusion rate and determine the pore volume in ultra-micropores, CO_2 adsorption at 273 K is recommended¹⁹. CO_2 has a higher diffusion rate and accelerated adsorption equilibrium. CO_2 has a saturation pressure of 26,400 Torr at 273 K and CO_2 adsorption starts at relative pressure of about 10^{-4} which can diffuse into the narrowest micropores up to 1.5 nm³⁹. The combination of CO_2 adsorption analysis results combined with the N_2 adsorption analysis is used for the full range characterization.

2.6 Activated carbon

One of the oldest and the most accepted industrial adsorbents are activated carbons with large surface areas per weight. Activated carbon is produced by combustion, partial combustion, or thermal decomposition of carbonaceous materials⁴⁵. The structure of activated carbon is a

combination of an amorphous structure and a graphite-like microcrystalline structure that forms a series of slit-shaped channels. The micro-crystallite layers of activated carbon are randomly oriented and less ordered and the interlayer spacing of activated carbon (0.34-0.35 nm) is larger than that of graphite, 0.335 nm. This microcrystalline, known as turbostratic, is built up during the carbonization process and impacted by carbonization conditions⁴⁶.

This random orientation in micro-crystallite layers is formed by the presence of heteroatoms such as oxygen, nitrogen and hydrogen, and by the defects in the carbon structure⁴⁷. The heteroatoms are bonded to carbon at the edges and corners of the aromatic sheets, or attached to carbon atoms at defect sites⁴⁷. Porosity of activated carbon depends on the nature of precursors, carbonization process and activating agent and conditions. Carbonization burns off most of the non-carbon species and produces char with non-porous structure and high content of carbon. Activation of char with an oxidation agent like steam, CO₂ or potassium hydroxide (KOH) results in development of internal surface area of char and removal of carbon atoms by reaction with oxidation agent at high temperature which forms an extended porous structure⁴⁷. Porosity is a function of the activating agent, conditions (temperature, flow rate and mass ratio of carbon to oxygen) and carbon burn-off^{45,48}.

The economic viability of the activated carbon as an adsorbent relies on its capacity, selectivity and stability in multi cycles adsorption process. The adsorption capacity mostly depends on porosity but selectivity is also a function of surface chemistry of the activated carbon. Carbon-oxygen functional groups are known to have the most impact on activated carbon characteristics such as the wettability, acidity, and selectivity. Precursors, such as biomass, are usually rich in oxygen and the nature of the precursors is an important factor in formation of oxygen-carbon surface groups. The heteroatoms are also introduced during the carbonization and activation process⁴⁶. Oxygen functional groups on carbon surface are classified into three groups, acidic, basic and neutral groups. The impregnation of activated carbons with metal oxides can improve the adsorption characteristic and surface chemistry of activated carbon for gas adsorption⁴⁷.

2.6.1 Pyrolysis, biochar and activation

Pyrolysis is the thermal degradation process that is used for a variety of feedstock, from agricultural and forestry biomass to animal manure, to convert them to value-added products⁴⁹.

Chars (carbon-rich solids), gases (CO, CO₂, and CH₄, with smaller amounts of hydrogen, ethane, and ethylene) and tars (bio-oils) are the main products of this process^{49,50}. Pyrolysis processes are classified into two main groups, fast and slow pyrolysis. The main characteristic of fast pyrolysis processes are as follows: high heating rates of the feedstock, pyrolysis temperature ranging from 400 to 550 °C, short vapor residence time (0.5 to 10 s), and low particle size of biomass

Slow pyrolysis processes are known by the following characteristics: low heating rate of the feedstock, long solid residence time (30 min to several hours) and the pyrolysis temperature varies with the feedstock.

The yields of the pyrolysis products (bio-char, bio-oil and non-condensable gaseous products) and its characteristics depend on the nature of the biomass and the process conditions. Pyrolysis temperature, heating rate, gas flow rate and residence time are the most important factors in pyrolysis process, respectively⁵¹.

Biochar

Biochar is the nonvolatile solid residue from the carbonization of biomass in absence of oxygen. Biochar has a high carbon content and low surface area which is usually used for soil treatment⁵⁰. The production yield and characteristics of biochar depend on the production methods, and parameters like heating rate, temperature, residence time and moisture content of precursor can impact the final product. Usually slower heating rate, longer residence time and higher pressure result in larger yields of biochar. In addition to its agricultural application, as a soil amendment, biochar can be used as a precursor to produce activated carbon⁴⁹. Biochar can be produce from all biological resources including manures, marine and lignocellulosic biomass. Chemical properties of the produced biochar depend on the precursor and pyrolysis conditions and can exhibit a wide range of porosity, composition and chemistry⁵².

Char activation

Activated carbons are usually prepared from biochar using different activation methods such as steam activation, CO₂ activation, KOH activation and phosphoric acid (H₃PO₄) activation⁵³. The methods of activation can be divided into two types, physical activation or chemical activation depending on whether a gaseous or solid activating agent is used for activation. Different types of biochar are reported in the literature as a precursor for activated carbon production^{49,54,55}. A summary of precursors, pyrolysis methods, activating agents and application of produced activated carbon is provided in Table 2-4.

Physical activation

Oxidation agents such as steam, CO₂ or mixture of both are used at mild temperature at 700-950 °C for physical activation of char. In this process, steam and CO₂ remove carbon atoms via formation of CO+H₂ or CO⁵⁶.

Steam is the most common activating agent. In this process, steam penetrates to the internal structure of the char and reacts with carbon that results in pore opening. With the further widening of pores, carbon pore walls collapse and results in formation of mesopores in steam activated carbon^{57,58} (Eq. 2-14 to 2-16).



Reactions **2-15** and **2-16** are exothermic, and reaction **2-14** is endothermic. This endothermic nature of the reactions facilitates the control of water-gas reaction.

In CO₂ activation, CO₂ is used as oxidizing agent to penetrate into the char; and selectively eliminates carbon atom, creates porosity and releases carbon monoxide (Eq. 2-17):



Table 2-4: Summary of different feedstocks, pyrolysis methods, activating agents and their applications

Precursor	Pyrolysis method	Activating agent	Application	Surface Area (m ² /g)	Pore volume (cm ³ /g)	Ref.
<ul style="list-style-type: none"> • grass cuttings • horse manure • beer waste • bio-sludge 	hydrothermally carbonization	CO ₂	CO ₂ adsorption	841 749 622 489	0.379 0.816 0.317 0.387	54
pine nut shell	slow pyrolysis	KOH	CO ₂ adsorption	NA	NA	55
Kernel shell	slow pyrolysis	KOH	N/A	17 -217	0.016-0.12	59
Teak saw dust	vacuum slow pyrolysis	steam	N/A	439-1150	NA	60
rubberwood saw dust	slow pyrolysis	steam	N/A	279-1095	NA	61
<ul style="list-style-type: none"> • Broiler litter • Soybean straw • 0.96Guayule shrub • Guayule bagasse 	fast pyrolysis	Steam	Metal ion adsorption(Cu ²⁺ , Cd ²⁺ , Ni ²⁺ , and Zn ²⁺)	<ul style="list-style-type: none"> • 136 • 204 • 293 • 249 • 455 • 716 • 535 	<ul style="list-style-type: none"> • 0.052 • 0.077 • 0.112 • 0.113 • 0.174 • 0.318 • 0.213 • 0.344 	62

<ul style="list-style-type: none"> • Corn stover • Corn cob • Switchgrass • Alfalfa stems 				• 793		
peanut hulls	unknown	steam ZnCl ₂ KOH H ₃ PO ₄	N/A	97-253	0.053-0.223	63
pistachio-nut shells	slow pyrolysis	steam	N/A	639-1015	NA	64
corn cobs	slow pyrolysis	steam H ₃ PO ₄		607-960	0.296-0.629	65

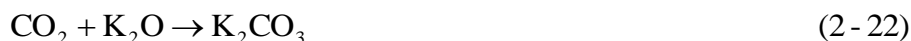
Chemical activation

Chemical activation with hydroxides such as KOH and sodium hydroxide (NaOH) gives rise to surface area and pore volume and is used to produce activated carbon with a highly developed porosity of micropores and some small mesopores⁵⁷. KOH activation was first proposed in 1978 by Wennerberg and O'Grady⁶⁶. KOH melts down at 360 °C. Chemical activation is usually carried out by mixing char with chemical activating agent followed by the carbonization under inert gas at 400–900 °C. Then sample is washed with acid and water to remove the remaining impregnating agent and salts and open the pores⁵⁷. The reduction of KOH to potassium as shown in Eq. 2-18^{66,67} results in the development of porous structure in KOH chemical activation:



The free metallic potassium (K) penetrates between lattices of the carbon. Formation of intercalated potassium resulted in the stretching of the lattice. With increasing temperature, the intercalated potassium is then removed from the graphitic structure resulting in extended micro

porosity^{57,66}. The main products of reaction below 700 °C are hydrogen, water, carbon monoxide, carbon dioxide, potassium oxide and carbonate (Eq. 2-19 to 2-22)⁶⁶:



Although the activation starts with these reactions (Eq. 2-19 to 2-22), it further proceeds with the following reactions to form the metallic potassium at temperatures above 700 °C (Eq. 2-23 and 2-24)⁶⁶:



The pore size distribution of the produced activated carbon depends on the nature of the biochar, activating agent, mass ratio of KOH to carbon, temperature, resident time and flow rate. Because the solid–hydroxide reactivity of the solid is a key factor in this process, the nature of the precursors are very important⁶⁷. Mass ratio of KOH to carbon and temperature are the controlling factors to maximize the ratio of ultra micropores to micropores in this reactions^{57,66}. The activation conditions for KOH activation in this work is adopted from a previous work using a similar experimental setup⁵⁷.

2.6.2 Surface chemistry of activated carbon

The microcrystalline structure in activated carbon is formed randomly and it has defects and/or partial burned graphitic layers in the crystallite, a variation in arrangement of electron clouds developed in carbon structure. The creation of unpaired electrons and incomplete saturated valance⁴⁷ due to formation of these electron clouds affect the adsorption properties of the activated carbon. Besides, heteroatoms are important parameters to form the chemical structure

of activated carbon. They bond to carbon atom at the edge and/or corner of the aromatic sheets/ defect points to form surface functional groups. Carbon-oxygen functional groups are undoubtedly the main functional groups due to their abundant quantities that significantly impact polarity, acidity, wettability and catalytic reactivity of activated carbons⁶⁸. Carboxyls, lactones, phenols, quinones and hydro-quinones are the main oxygen functional groups in carbon structure. Carboxyls, lactones, phenols are known as weakly acidic groups of Brönsted-type acid base reactions. The acidic surface functional groups are not thermally stable and decompose with heat treatment in inert gas in temperature range of 320-750°C.

Although the structure of the basic functional groups is not completely understood, pyrone, chromene, and quinone are categorized as basic functional groups. “In ammonia/amine treatment, nitrogen can replace the oxygen in ether-type functional groups and increases the basic characteristic of the surface”^{47,57}.

2.6.3 Adsorption on activated carbons

Regardless of preparation techniques and activation conditions, activated carbons usually exhibit lower adsorption capacities as compared to zeolites or molecular sieves under low partial pressure of CO₂⁶⁹⁻⁷¹. However, activated carbon adsorbents are fully regenerated at 100-150 °C while zeolite usually cannot gain their initial adsorption capacity. Activated carbons are low cost and thermally stable adsorbents that are less affected by the presence of moisture in the gas mixture^{72,73}. On the other hand, CO₂ uptake decrease with temperature due to the exothermic nature of CO₂ adsorption⁷⁴⁻⁷⁶. A summary of CO₂ adsorption conditions and capacity of activated carbon and other solid adsorbent materials in the literature are provided in Table 2-5⁷⁷.

Amine /ammonia treatment of activated carbon is the most common technique to improve CO₂ adsorption performance of activated carbon. Activated carbon treated with ammonia gas at temperatures >200 °C showed a larger CO₂ adsorption capacity as compared to the un-treated activated carbons⁷⁸; this was attributed to the introduction of nitrogen- containing functional groups onto the carbon surface. Zhang et al.⁷⁹ found that the impregnation of activated carbon with poly ethyleneimine (PEI) could enhance the CO₂ adsorption capacity of activated carbons up to 2.13 mmol g⁻¹ at 75 °C. Similar results are reported in the literature^{16,58,79}. However, the

amine impregnation causes a significant decrease of the surface areas and pore volume due to the pore filling / blockage on carbon surface.

Table 2-5: CO₂ adsorption capacity of activated carbons

Adsorbent	Adsorption temperature(K)	CO ₂ Pressure (Bar)	CO ₂ adsorption capacity (mmol/g)	Ref
Activated carbon	298	1	2.07	80
Activated carbon	298	0.1	1.1	74
	328	0.1	1.1	
	298	1	3.2	
	328	1	1.6	
Activated carbon	298	0.2	0.75	75
	373	0.2	0.1	
Activated carbon	288	1	2.45	71
AC Norit RB1	294.2	0.1	2.456	81
	294.2	0.8	6.027	
	311.2	0.1	1.759	
	329.6	0.1	1.263	
	348.3 K	0.1	0.911	
Activated carbon (RB)	303	1	1.39	76
Activated carbon (MSC V)	303	1	1.82	
Activated carbon (BPL)	303	1	1.93	
Activated carbon (horse manure)	273	0.1	1.36	54
Activated carbon (grass cuttings)	273	0.1	1.45	
Activated carbon (beer waste)	273	0.1	1.31	
Activated carbon (biosludge)	273	0.1	0.84	
Activated carbon (beer waste)	273	0.1	0.8	
Zeolite 13X	293	0.15	2.63	77

Zeolite 13X	295	1	4.61
Zeolite 13X	298	1	4.66
Molecular sieve 13X	298	1	2.8-3.6
Molecular sieve 4A	298	1	2.3-3.1
Silicalite	303	0.15	0.45
K ₂ CO ₃	373	0.35	2.1
Na ₂ CO ₃	333-343	0.1-0.4	0.5-3.2

Adsorption cycles

In addition to adsorption capacity and selectivity, the long-term stability and regenerability of the adsorbents are important characteristic. Three main regeneration methods are temperature swing adsorption (TSA), pressure swing adsorption (PSA) and vacuum swing adsorption (VSA). The CO₂ adsorption on activated carbon is principally “attributable to physical force, which makes the regeneration process of CO₂ at a relatively low temperature feasible in TSA”⁸².

Figure 2-8 shows the schematic of TSA in which a gas steam of component i at partial pressure of p_i flows through the packed-bed at T_1 to reach equilibrium (q_1). For bed regeneration, the bed temperature is increased to T_2 and desorption process is continued to reach the second equilibrium at q_2 ($q_2 < q_1$). In a dual-bed system, the adsorption and desorption time must be equal. Therefore, the full regeneration to the initial capacity is not always possible.

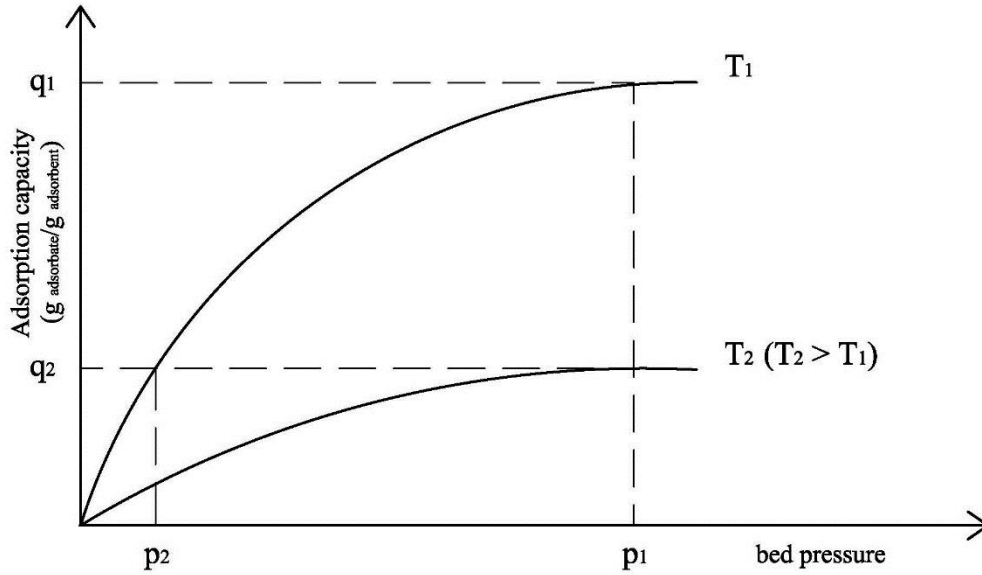


Figure 2-7: Temperature swing adsorption

2.7 Mass transfer model

The mechanism of CO₂ transport from a gas mixture to the active sites on the adsorbent surface and physical adsorption includes three main stages through the packed-bed: External bulk mass transfer through the film surrounding the particles, diffusion through the pores and adsorption. They are explained in details below:

Bulk mass transfer

Moisture in the flue gas and air results in the formation of the fluid film around the particles or pellets through which molecular diffusion of CO₂ occurs. This step is represented by the mass transfer coefficient of the film, according to the linear law of Fick (Eq. 2-25)¹⁹:

$$N_{f,i} = k_{f,i}(C_{i,b} - C_{i,s}) \quad (2-25)$$

where $N_{f,i}$ is the mass flux, $k_{f,i}$ is the mass transfer coefficient, $C_{b,i}$ is the bulk concentration of component i and $C_{i,s}$ is the component i concentration at the surface of the particle.

Several studies reported heat and mass transfer coefficient data in packed beds^{83–86}. For a Reynolds number 3-10000, Wakao and Funazkri⁸⁴ collected data of evaporation of water, evaporation of organic solvent, sublimation of naphthalene and dissolution of solid in a packed bed. The developed correlation for packed bed is described as (Eq. 2-26 to 2-29):

$$Sh_i = 2 + 1.1Re^{0.6}Sc_i^{1/3} \quad (2 - 26)$$

In this correlation:

$$Sh_i = \frac{k_{f,i}d_p}{D_{m,i}} \quad (2 - 27)$$

$$Sc_i = \frac{\eta_f}{\rho_f D_{m,i}} \quad (2 - 28)$$

$$Re = \frac{\rho_f u d_p}{\varepsilon_b \eta_f} \quad (2 - 29)$$

where d_p is the particle diameter, $D_{m,i}$ is the molecular diffusion coefficient, η_f is the fluid viscosity, ρ_f is the fluid density, $k_{f,i}$ is the mass transfer coefficient, u is the superficial velocity and ε_b is the bed porosity. In this equation, density of the gas mixture is defined as (Eq. 2-30 and 2-31):

$$\rho_f = \sum_i y_i \rho_i \quad (2 - 30)$$

$$\rho_i = \frac{M_i P}{RT} \quad (2 - 31)$$

Viscosity of binary mixture at low pressures is determined by the method of Wilke (Eq. 2-32 to Eq. 2-35)⁸⁷:

$$\eta_f = \frac{\sum_{i=1}^n y_i \eta_i}{\sum_{\substack{j=1 \\ j \neq i}}^n y_i \phi_{ij}} \quad (2 - 32)$$

$$\varphi_{ij} = \frac{1}{\sqrt{8\left(1 + \frac{M_i}{M_j}\right)^{1/2}}} \left[1 + \left(\frac{\eta_i}{\eta_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2 \quad (2-33)$$

$$\varphi_{ji} = \frac{\eta_j}{\eta_i} \frac{M_i}{M_j} \varphi_{ij} \quad (2-34)$$

$$\eta_i = X_i + Y_i T + Z_i T^2 \quad (2-35)$$

where y_i is the mole fraction of component i , M_i and M_j are the molecular weight of component i and j , respectively, T is the temperature (K), X , Y , and Z are regression coefficients for chemical compound and η_i is the viscosity of component i . X , Y and Z for CO_2 and N_2 are shown in Table 2-6:

Table 2-6: Regression coefficients of viscosity calculation for CO_2 and N_2

	CO_2	N_2
X	11.811	42.606
Y	4.98E-01	4.75E-01
Z	-1.09E-04	-9.88E-05

Bed porosity is approximated “by the ratio between the total volume of void space between the particles and the volume of the bed”⁸⁸ as follows (Eq. 2-36):

$$\varepsilon_b = \frac{V_b - \sum V_p}{V_b} = 1 - \frac{\rho_b}{\rho_p} = 1 - \frac{W/V_b}{\rho_p} \quad (2-36)$$

where W is weight of the bed, V_b is volume of the bed and ρ_p is the particle density or apparent density which is defined as the ratio of weight of the bed to the volume measured including the pore volume as well as the void spaces of the particle. Particle density is approximated based on

the skeletal density (true density) and pore volume determined by N₂ and CO₂ adsorption data (pore size distribution) as follows (Eq. 2-37)⁸⁸:

$$V_{p,b} = \frac{1}{\rho_p} - \frac{1}{\rho_s} \quad (2-37)$$

Skeletal density in this equation is defined as a ratio of the mass of solid to the solid volume measured excluding the pores and the void spaces.

2.7.1 Internal mass transfer

From the surface on the particles, the gas molecules diffuse into the micro/meso/macro pore networks and then adsorb on the internal surface of the particles. To understand the mass transfer mechanism and find the resistance step a mass transfer model is required to recognize which resistance dominates. Various kinetic models have been developed in the past. Linear driving force (LDF)⁸⁹ model with an effective diffusion coefficient is believed to be the earliest adsorption model pertaining the adsorption rate based on the adsorption capacity (Eq. 2-38)⁹⁰.

$$\frac{\partial q}{\partial t} = k_{LDF}(q^* - \bar{q}) = \frac{15D_{pi}}{R_p^2}(q^* - \bar{q}) \quad (2-38)$$

where K_{LDF} is the mass transfer coefficient, q^* is equilibrium concentration at the surface of the particle (mol of adsorbate/mass of particle), \bar{q} is the mean solid concentration over the particle volume (mol of adsorbate/mass of particle), D_{pi} is the particle diffusion coefficient (m²/min) and R_p is the particle radius (m). This model for bi-porous adsorbents, where both macro-pore and micropores are important, is not accurate. In the later models^{91,92} for bi-porous structures, the adsorption rate was described by both mass transfer resistance in micropores and macro-pores. These models are also restricted by adsorbate concentration. At high concentration where the impact of viscous flow and surface diffusion are significant, these models fail. Surface diffusion is also becomes important in adsorbents with large surface area. To model adsorption rate in a range of operating conditions, all these mass transfer mechanisms must be considered. For CO₂ adsorption, the CO₂ concentration is usually below 20 mol% and the impact of viscose flow is negligible.

2.7.2 Bi-linear driving force model

In this work, the Bi-linear Driving Force (Bi-LDF) model proposed by Grande and Rodrigues⁹³ is used which includes a combination of molecular diffusion and Knudsen and surface diffusion. Bulk and Knudsen diffusion occur together while surface diffusion occurs in parallel to these two mechanisms (Figure 2-9). This model describes all three mass transfer mechanism⁹⁴.

Bulk mass transfer is due to the molecule-molecule collisions and in large pore and/or at high concentration becomes more important.

Knudsen diffusion is due to the molecule-pore wall collisions and “when the mean free path of the gas molecule is larger than the pore diameter becomes important”¹⁹.

Surface diffusion is due to the diffusion of the adsorbed molecule along the surface of pore wall and it becomes important at high concentration or high surface area. In ultra micropores, “the diffusing molecules never escape the potential field of the adsorbing surface and the transport involves the adsorbed molecules “hopping” across the adsorption sites”⁹⁵.

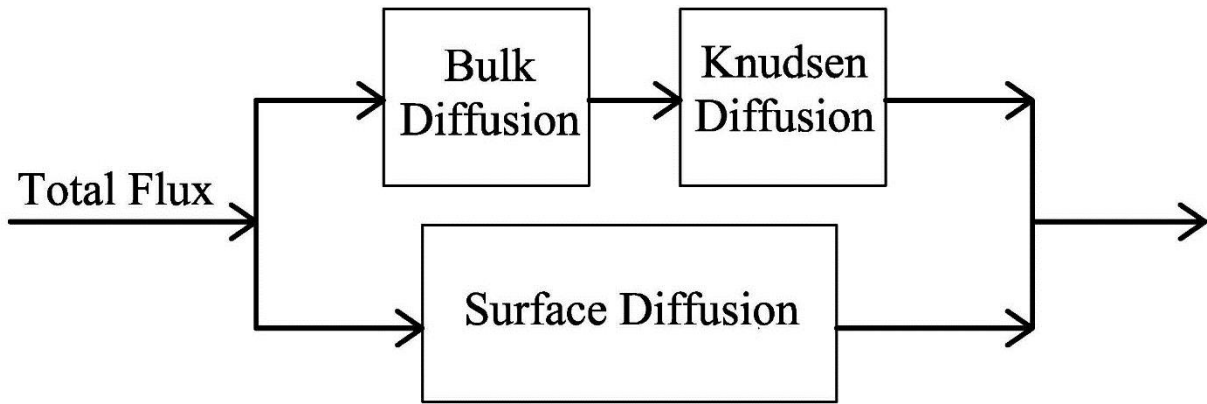


Figure 2-8: Diffusion mechanism in bi-porous material at low concentration

In Bi-LDF model, an effective LDF coefficient is proposed to combine the molecular and Knudsen diffusion rate (Eq. 2-39 to Eq. 2-41).

$$\frac{\partial c_{pi}}{\partial t} = k_{pi}(c_i - \bar{c}_{pi}) \quad (2-39)$$

$$k_{pi} = \frac{15\varepsilon_p D_{pi}}{R_p^2} \frac{Bi_i}{Bi_i + 1} \quad (2-40)$$

$$Bi_i = \frac{R_p k_{f,i}}{5\varepsilon_p D_{pi}} \quad (2-41)$$

In Eq. 2-41, the ratio of internal macropore to the external film resistance is determined by Bi_i , the Biot number, and D_{pi} represents the effective macropore diffusivity corrected for the tortuosity of component i ⁹⁶. D_{pi} is calculated as follows (Eq. 2-42)^{87,97}:

$$\frac{1}{D_{pi}} = \frac{1}{D_{K,i}} + \frac{1}{D_{m,i}} \quad (2-42)$$

In this equation $D_{K,i}$ is the Knudsen diffusivity and $D_{m,i}$ is the macropore diffusivity. Knudsen diffusivity is calculated as follows (Eq. 2-43)⁹⁷:

$$D_{K,i} = \frac{d_p \varepsilon_p}{3\tau_K} \sqrt{\frac{8RT}{\pi M_i}} \quad (2-43)$$

where τ_K is the tortuosity factor^{98,99} as follows (Eq. 2-44):

$$\tau_K = \frac{\varepsilon_p}{0.4\varepsilon_p - 0.0328} \quad (2-44)$$

The macropore diffusivity in a binary mixture is calculated as follows (Eq. 2-45 to 2-47)^{98,99}:

$$D_{m,i} = \frac{(1 - y_i)}{\sum_{\substack{j=1 \\ j \neq i}} \frac{y_j}{D_{i,j}}} \quad (2-45)$$

$$D_{i,j} = \frac{\varepsilon_p D_{i,j}^0}{\tau} \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right)^{1.75} \quad (2-46)$$

$$\tau = 1 + 0.5(1 - \varepsilon_p) \quad (2-47)$$

“For the micropores, the Darken equation, one of the earliest models to describe surface diffusion, is used to describe the concentration dependence of micropore diffusivity”^{96,100}(Eq. 2-48).

$$\frac{\partial q_{ci}}{\partial t} = \frac{15D_{ci}}{r_c^2} (1 - \varepsilon_p) \rho_p (q_{ci}^* - \bar{q}_{ci}) \quad (2-48)$$

In this equation, “ D_{ci} is the crystal diffusivity, r_c is the crystal radius, q_{ci}^* is the adsorbed phase concentration in equilibrium with concentration of component i over the particle and \bar{q}_{ci} is the averaged adsorbed phase concentration”¹⁰¹.

Adsorption on heterogeneous adsorbents can be well described by a Langmuir model (Eq. 2-49)

$$q_{ci}^* = \frac{q_{si} b_i p_i}{1 + b_i p_i} \quad (2-49)$$

where q_{si} is the saturation capacity of adsorbate i , and b_i is the temperature-dependent isotherm constants as follows (Eq. 2-50):

$$b_i(T) = b_i(T_0) \exp\left(\frac{-\Delta H_{ads,i}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (2-50)$$

The crystal diffusivity at any loading is a function of surface diffusion at zero loading multiplied by the thermodynamic correction factor of $\frac{\partial \ln p_i}{\partial \ln q_{ci}}$ (Eq. 2-51)^{46,96}.

$$D_{ci} = D_{ci}^\infty \frac{d \ln(p_i)}{d \ln(q_{ci})} \bigg|_T \quad (2-51)$$

“Crystal diffusivity of the adsorbed molecule in micropores can be explained as an activated process”^{101,102}(Eq. 2-52):

$$D_{ci}^\infty = D_{ci0} \exp\left(\frac{-E_{ai}}{RT}\right) \quad (2-52)$$

The exponential term in this equation “expresses the probability of a molecule to have sufficient kinetic energy to surmount the energy barrier”¹⁰²; where, D_{ci0} is the limiting diffusivity at high temperature and $E_{a,i}$ is the activation energy. For a Langmuir isotherm, the thermodynamic factor of $\frac{\partial \ln p_i}{\partial \ln q_{ci}}$ is calculated as (Eq. 2-53)^{96,103}:

$$\left. \frac{d \ln(p_i)}{d \ln(q_{ci})} \right|_T = \frac{1}{1-\theta} = \frac{1}{1-q_{ci}^*/q_{si}} \quad (2-53)$$

An overall adsorption in a particle can be described as (Eq. 2-54):

$$\rho_p \bar{q}_{pi} = \epsilon_p c_{pi} + (1 - \epsilon_p) \rho_s \bar{q}_{ci} \quad (2-54)$$

where ρ_s is the skeletal density, ρ_p is the apparent density, ϵ_p is the particle porosity, c_{pi} is the concentration of component i in the macropores, q_{pi} is the averaged adsorbate concentration of component i per unit adsorbent particle mass⁹⁶ (mol/g) and q_{ci} is the averaged adsorbate concentration of component i per unit crystal mass⁹⁶ (mol/g). Therefore, combining the Eq. 2-48 and 2-54 results in an overall adsorption using the bi-LDF rate equation(Eq. 2-55)¹⁰¹:

$$\rho_p \frac{\partial \bar{q}_{pi}}{\partial t} = k_{pi}(c_i - \bar{c}_{pi}) + \frac{15D_{ci}}{r_c^2} (1 - \epsilon_p) \rho_s (q_{ci}^* - \bar{q}_{ci}) \quad (2-55)$$

If the radial gradients in pressure and concentration of the gases in the solid and the gas are negligible, the overall mass balance for the packed-bed can be written as (Eq. 2-56):

$$\epsilon_t \frac{\partial c_i}{\partial t} + (1 - \epsilon_b) \rho_s \frac{\partial \bar{q}_{pi}}{\partial t} = -\epsilon_b \frac{\partial u c_i}{\partial z} + \epsilon_b \frac{\partial}{\partial z} \left(D_{ax} \frac{\partial c_i}{\partial z} \right) \quad (2-56)$$

Combining **Eq. 2-55** and **2-56** results in (**Eq. 2-57**):

$$\epsilon_t \frac{\partial c_i}{\partial t} + (1 - \epsilon_b) \left[k_{pi}(c_i - \bar{c}_{pi}) + \frac{15D_{ci}}{r_c^2} (1 - \epsilon_p) \rho_s (q_{ci}^* - \bar{q}_{ci}) \right] = -\epsilon_b u \frac{\partial c_i}{\partial z} + \epsilon_b \frac{\partial}{\partial z} \left(D_{ax,i} \frac{\partial c_i}{\partial z} \right) \quad (2-57)$$

“where D_{ax} is the axial dispersion coefficient, u is the superficial velocity in bed, z is the axial distance variable, t is the time, ε_b is the bed porosity”¹⁹ and ε_t is the total porosity of the packed bed. In this equation, the following terms exist:

Diffusion term $\varepsilon_b \frac{\partial}{\partial z} \left(D_{ax} \frac{\partial c_i}{\partial z} \right)$:

Since axial mixing reduces the separation efficiency and it is not an undesirable term, minimizing this term is one of the main concerns to enhance the separation factor¹⁹. Molecular diffusion and turbulent mixing are known as the main driving forces of axial dispersion in a packed bed¹⁹. Gas velocity determines that either molecular diffusion or turbulent mixing is dominant. The axial Peclet number for flow around the particle describes axial dispersion in the gas flow (Eq. 2-58):

$$\frac{1}{Pe} = \frac{D_{ax}}{ud_p} \quad (2-58)$$

where u is the gas superficial velocity and d_p is the particle diameter. Wakao and Funazkri⁸⁴ developed the following equation for $Re > 5$ (Eq. 2-59):

$$\frac{\varepsilon_b D_{ax}}{D_{m,i}} = 20 + 0.5(Sc)(Re) \quad (2-59)$$

This equation is valid for evaporation, sublimation, dissolution or a diffusion controlled chemical reaction in non-porous surfaces. Although this equation does not exactly fit the adsorption process in porous beds, it can be used with some error to estimate the axial dispersion for gas adsorption in porous beds^{96,101,104}.

Convection term $\frac{\partial uc_i}{\partial z}$: This term represents the advection or bulk mass transfer of substances in the z direction due to motion of a gas over the surface.

Accumulation term $\frac{\partial c_i}{\partial t}$: This term accounts for the changes in mass/ concentration of component i per unit of time.

Adsorption term $\frac{\partial \overline{q_{pi}}}{\partial t}$: This term shows mass transfer from the gas phase to the solid phase as explained above.

2.8 Error analysis of experimental results

Since most of the results in this thesis are experimental basis and there is always a margin of doubt in any measurement, error in experiment for experimental analysis have been calculated and average results are reported¹⁰⁵.

$$\text{Standard Deviation} = \sqrt{\frac{1}{M(N-1)} \sum_{j=1}^M \sum_{i=1}^N (x_{ij} - \overline{x_j})^2} \quad (2-60)$$

$$\overline{x_j} = \frac{1}{N} \sum_{i=1}^N x_{ij} \quad (2-61)$$

$$\text{Degree of freedom} = M(N-1)$$

where

M: Number of series of analyses

N: number of measurements in each series of analyses

X_{ij}: the observed values of the sample

$\overline{x_j}$: the mean value of these observation

2.9 Summary

The ideal adsorbent for CO₂ separation should have some important characteristics such as high cyclic CO₂ adsorption capacity, appropriate selectivity over N₂ and O₂ and high stability in repetitive cyclic adsorption/desorption process. Due to huge volume of flue gas, capital cost of post-combustion process is large. So, using expensive sorbent materials or materials with high disposal expenses can escalate cost related to the process and make it economically unfeasible. This research focused on development of low-cost and effective adsorbents for CO₂ capture from coal-fired power plants.

Chapter 3 Study of the Impact of Activating Agents on Activated Carbons for CO₂ Adsorption

A similar version of this chapter has been published in the Journal of Environmental Sciences.

- *Shahkarami, S.; Azargohar, R.; Dalai, A. K.; Soltan, J. Breakthrough CO₂ Adsorption in Bio-Based Activated Carbons. J. Environ. Sci. 2015, 34, 68-76.*

In addition, some parts of this chapter were presented at the following conferences and symposiums:

- Enhanced CO₂ Adsorption on Activated Carbon, 66th Canadian Chemical Engineering Conference, Quebec City, QC, October 16-19, 2016.
- Selective CO₂ Adsorption on Activated Carbons, 24th Canadian Symposium on Catalysis Ottawa, ON, Canada, May 8-11, 2016.
- CO₂ Capture on Bio-based Activated Carbons, Biorefinery I- Chemicals and Materials from thermo Chemical Biomass, Chania, Greece, September 27-October 2, 2015.
- Development of Activated Carbon Adsorbents for CO₂ Capture, 64rd Canadian Chemical Engineering Conference, Niagara Falls, ON, Canada, October 19-22 2014.

- Study the Performance of Bio-based Activated Carbons for CO₂ Capture, 63rd Canadian Chemical Engineering Conference, Fredericton, NB, Canada, October 20-23, 2013.

Contribution of the Ph.D. candidate

The bench-scale adsorption set-up was designed and installed by Sepideh Shahkarami. A LabVIEW program for accurate data recording was designed and linked to the adsorption set-up by Sepideh Shahkarami. The activation conditions were selected by Sepideh Shahkarami with assistance from Dr. Ramin Azargohar. The experimental design (in Design-Expert® software V9) were planned and experiments were conducted by Sepideh Shahkarami. All the sample characterizations were performed and the related data were analyzed by Sepideh Shahkarami. The data analyses and interpretations were conducted by Sepideh Shahkarami. All of the written text was prepared by Sepideh Shahkarami and all the experiments were discussed with Drs. A.K. Dalai and J. Soltan.

Contribution of this chapter to the overall study

In order to develop an optimized activated carbon adsorbent with high CO₂ uptake, it was necessary to study the impact of activating agent on CO₂ adsorption performance of activated carbons. In this part of research, the main focus was on the impacts of activating agents on the porosity and surface chemistry of activated carbon as well as CO₂ adsorption performance of the produced activated carbons under different adsorption conditions.

Abstract

In this work, the effects of different methods of activation on CO₂ adsorption performance of activated carbon were studied. Activated carbons were prepared from biochar, obtained from fast pyrolysis of white wood, using three different activation methods of steam activation, CO₂ activation and KOH activation. CO₂ adsorption behavior of the produced activated carbons were studied in a fixed-bed reactor set-up at atmospheric pressure, temperature range of 25-65°C and inlet CO₂ concentrations range of 10-30 mol.% in He to determine the effects of the surface area, porosity and surface chemistry on adsorption capacity of the samples. Characterization of the micropore and mesopore texture was carried out using N₂ and CO₂ adsorption at 77 and 273 K,

respectively. Central composite design was used to evaluate the combined effects of temperature and concentration of CO₂ on the adsorption behavior of the adsorbents. The KOH activated carbon with total micropore volume of 0.62 cm³/g and surface area of 1400 m²/g had the highest CO₂ adsorption capacity of 1.8 mol/kg due to its microporous structure and high surface area under the optimized experimental conditions of 30 mol.% CO₂ and 25°C. The performance of the adsorbents in multi-cyclic adsorption process was also assessed and the adsorption capacity of KOH and CO₂ activated carbons remained remarkably stable after 50 cycles with low temperature (160°C) regeneration.

3.1 Introduction

Activated carbons are known to have large adsorption capacity for CO₂ and they can be produced from low cost and abundant precursors such as bio-char³¹. It has been shown that surface area and pore size distribution of activated carbon affect CO₂ capture performance of activated carbon¹⁰⁶. Moreover, starting precursors have a significant effect on CO₂ adsorption behavior of activated carbons^{47,55}. However, a comparison of different methods of activation of biochar on its CO₂ adsorption performance has not been reported before. This work focused on the effect of different activation methods on porosity, surface area and adsorption capacity of the activated carbons to explain CO₂ adsorption behavior in activated carbons. Steam, CO₂ and KOH were used as activating agents for activation of biochar obtained from fast pyrolysis of whitewood.

The main challenge of post combustion carbon capture processes is operation at low concentration of CO₂⁸². In this work, the CO₂ adsorption performance of the adsorbents was investigated at atmospheric pressure, temperatures range of 25-65 °C and CO₂ concentrations (C_{CO₂}) range of 10-30 mol. % and the influence of activation method, porous structure, surface area and surface chemistry on performance of the adsorbents were studied. Adsorption capacity was analyzed using breakthrough curve in an isothermal fixed-bed reactor and the bed adsorption capacity was studied as a function of both breakthrough time and the S-shape of the breakthrough curve under the designed operating conditions. Central composite design (CCD) method was applied for experimental design to find optimized process conditions and second-order models were developed to predict the adsorption capacity of adsorbents as functions of temperature and

concentration of CO₂ in inlet stream. These models showed the significance of variables and the interactions among them on the CO₂ adsorption process.

3.2 Materials and methods

3.2.1 Biochar

The biochar used in this study was a by-product of fast pyrolysis of whitewood provided by Dynamotive Energy Systems Corporation (BC, Canada). According to the manufacturer, the operating conditions for this process were 500°C, atmospheric pressure and residence time less than 1 sec. The biochar yield of this process was 10-15 wt. %. The as-received biochar was sieved, and particle size range of 178-710 µm was collected for activation processes.

3.2.2 Physically activated carbon

Physically activated carbon was prepared using carbon dioxide and steam as activating agents. Before activation, sieved biochar was dried in air for 12 h at 110 °C. The process conditions of the steam and CO₂ activated carbon were chosen to obtain similar BET surface area and total pore volume in both products. The detailed information for activation set-up was described in Appendix A¹⁰⁷. The activation yield was calculated using the mass ratio of produced activated carbon to biochar.

Steam Activation

In each batch, 20 g of biochar was loaded into the reactor and heated to 700°C with the heating rate of 3°C/min while flowing nitrogen carrier gas at the flow rate of 140 standard mL/min. Steam was injected into the reactor with the steam-to-carbon mass ratio of 1.06 for 1.4 h. After the injection, the reactor was cooled down to room temperature under nitrogen flow. The yield of product was 55 wt. % in steam activation process.

CO₂ Activation

In each run, 15 g of biochar was placed in the fixed-bed reactor under an argon flow rate of 100 standard mL/min. The temperature of the reactor was increased to 890 °C with the heating rate of 3°C/min. Then, the gas was switched to CO₂ with the flow rate of 130 standard mL/min. After 100

min, the reactor was cooled down to room temperature under argon gas flow. The yield of product was 52 wt. % in CO₂ activation process.

The Schematic of experimental set-up, procedure and calibration are provided in Appendix A.

3.2.3 Chemically activated carbon

The physical activation set-up was also used for chemical activation of biochar. KOH was used as the activating agent. Biochar was impregnated with KOH in 100 mL of distilled water with carbon-to-KOH mass ratio of 0.81 on dry basis. After 4 h at the room temperature, the prepared mixture was dried in oven at 110°C for 12 h. 20 g of the dried sample was placed in the reactor under a nitrogen flow of 240 standard mL/min and was heated to 300°C with the heating rate of 3°C/min, and was held for 1 h at 300°C¹⁰⁸. Then, the temperature of the reactor was increased to 775°C with the heating rate of 3°C/min and held at this temperature for 2 h before cooling down to room temperature. In the next step, the sample was washed with hot water, followed by 0.1 M HCl, and finally by distilled water to remove the soluble salts and the potassium compounds^{109,110}. Then the sample was dried in oven overnight at 110°C in air. The product yield of chemical activation was 33 wt. %. The details of activation process, experimental set-up and calibrations are provided in Appendix A.

3.2.4 Characterization

Elemental analysis and ash content

The mass fractions of carbon, hydrogen, nitrogen and sulfur in the samples were determined from elemental analysis performed on a Vario EL III elemental analyzer (Vario EL III, Elementar, Germany). Oxygen content of samples was determined by difference. The ash contents of biochar and activated carbons were measured according to ASTM D2866 - 11.

BET surface area, pore volume and pore size distribution

The nitrogen adsorption isotherms of activated carbon samples at 77 K and BET (Brunauer-Emmett-Teller) surface area and total pore volume of the samples were determined using ASAP 2020 system (ASAP 2020, Micromeritics Instruments Inc., USA). The samples were degassed at

300°C to a vacuum of 550 $\mu\text{m Hg}$ prior to the analysis. The micropore size distribution was determined using the non-local Density Functional Theory (NLDFT)^{42,111} applying N_2 and CO_2 adsorption on slit-pore carbon¹¹² at 77 K and 273 K, respectively. Nitrogen at 77 K has a saturation pressure of 760 Torr and N_2 adsorption starts at relative pressure (P/P_0) between 10^{-7} and 10^{-5} whereas CO_2 has a saturation pressure of 26,400 Torr and CO_2 adsorption starts at relative pressure of about 10^{-4} . Since diffusion rates of N_2 and consequently attaining equilibrium in ultramicropores with diameter between 0.5 and 1 nm is very slow and requires very low relative pressure and high uptake of N_2 , CO_2 adsorption at 273K was used to overcome diffusion limitations¹⁹. The CO_2 analysis results were combined with the N_2 adsorption analysis for the full range characterization. IUPAC (International Union of Pure and Applied Chemistry) classification was considered for pore size distribution³⁰. Ultramicropores have pore width less than 0.7 nm, super-micropores show pore width between 0.7 and 2 nm, and mesopores have pore width between 2 and 50 nm.

X-ray photoelectron spectroscopy (XPS)

Surface chemistry of the activated carbon samples was studied and oxygenated functional groups on the surface were quantified using X-ray photoelectron spectroscopy. This was equipped with an omicron monochromatized Al $K\alpha$ source ($h\nu = 1486.7 \text{ eV}$) and SPHERA EA125 hemispherical electron energy analyzer in the Surface Science Facility at the Resonant Elastic and Inelastic X-ray Scattering (REIXS) beamline 10ID-2 of the Canadian Light Source (The Surface Science Facility, Canadian Light Source, Canada). The survey scan spectra were collected in the 0-1200 eV binding energy range in 0.5 eV steps with pass energy of 50 eV. High resolution scanning of the C1s region was also conducted in 0.1 eV steps with pass energy of 25 eV. An accelerating voltage of 15 kV and an emission current of 20 mA were used for the analysis. The operating pressure was less than 2×10^{-10} mbar. Peak deconvolutions of high-resolution C1s spectra were conducted using the Casa XPS software (version 2.3.16 PR 1.6).

3.2.5 Breakthrough CO_2 adsorption measurements

CO_2 adsorption was performed in an isothermal fixed-bed tubular reactor. A K-type thermocouple was placed inside the reactor and the reactor temperature was controlled using a heating tape and

a temperature controller (2416, Eurotherm, USA). The reactor was loaded with 5 g of activated carbon and pre-heated at 160°C for 2 h under helium (He) flow before the adsorption experiments. After cooling down the reactor to the desired operating temperature, the feed gas was switched from He to He/CO₂ gas mixture. The total feed flow rate was maintained constant at 50 standard mL/min in all experiments. The feed flow rates were controlled with mass flow controllers (5850E A/B, Brooks Instrument, USA). For continuous monitoring, the outlet gas flow rate was recorded and the dynamic CO₂ adsorption capacity was measured using a micro-gas chromatograph analyzer (CP-4900, Varian, USA) equipped with a thermal conductivity detector (TCD). The standard gas composition () and calibration curves are provided in Appendix B. The adsorption process was continued up to the saturation point where the outlet concentration of CO₂ reached the inlet concentration of CO₂. The schematic diagram of the set-up schematic is shown in **Fig. 3-1** and the details of the set-up and calculation methods are described in section 2.3.1 and Appendix B.

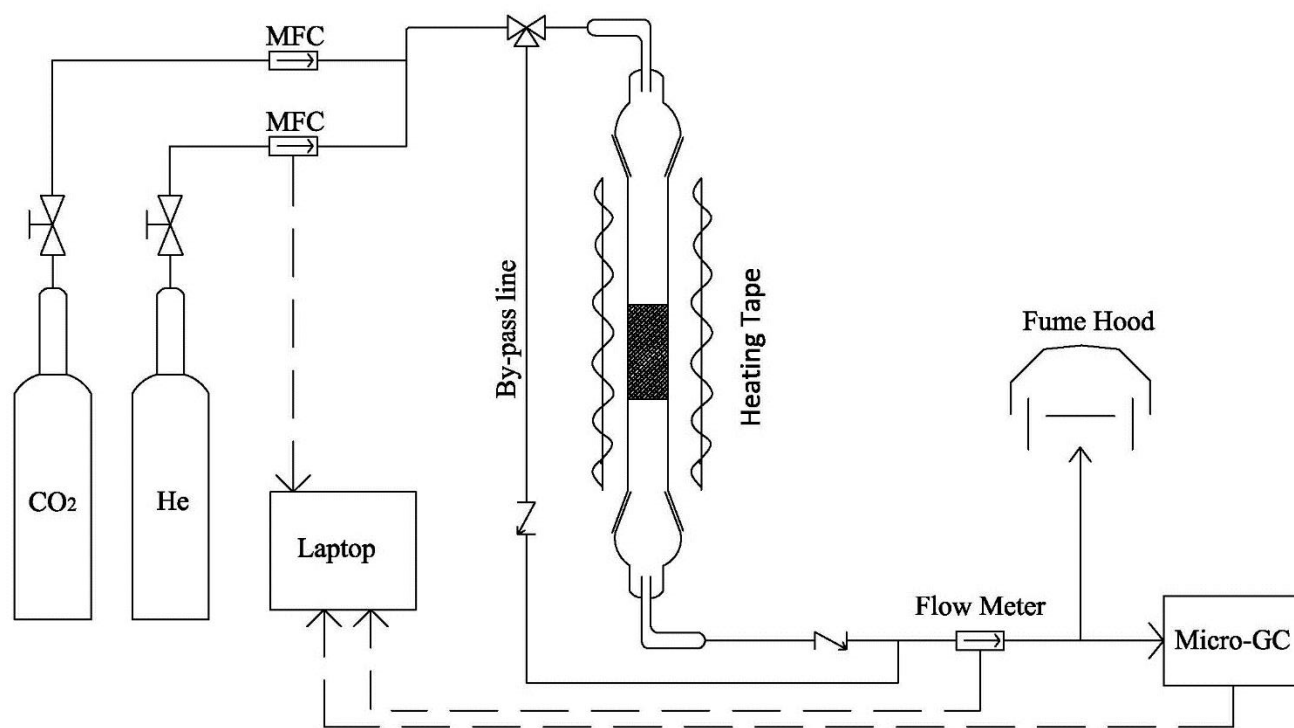


Figure 3-1: Schematic of adsorption set-up

The CO₂ adsorption process was studied using central composite design to optimize the process conditions and determine the interaction effect of parameters. For the experimental design, C_{CO₂} and temperature (*T*) were selected as experimental variables and they were studied at two levels of 10-30 mol.% and 25-65 °C, respectively. For a 2 level study, the total number of experiments is given as $2^n + 2n + n_c$ where *n* is the number of independent process variables and *n_c* is the number of center points or replicates used to estimate the residual error^{31,107}. Each center point adds one degree of freedom (df) from which the experimental error is estimated. Therefore, 14 experiments including 8 factorial and axial points as well as 6 replications at the center point were conducted for the adsorption process using each type of the activated carbons (ACs) (Table 3-3). The model helps to assess the responses in the variables space and to find the best region to reach the optimum response. The second-order model is used to estimate the response (Eq. 3-1):

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + \varepsilon \quad (3-1)$$

where *y* is the predicted response, β_0 is the constant, β_1 and β_2 are the linear coefficients, β_{11} and β_{22} are the quadratic coefficients, β_{12} is the interaction coefficients, *x₁* and *x₂* are the coded values of the parameters and ε is the residual error¹¹³. The model predicts the behavior of the response as a function of the variables and their interaction. The fitness of the model is evaluated using Analysis of Variance (ANOVA) and squared-R¹¹³. The response factors in this study are the CO₂ adsorption capacity and the breakthrough time (*t_b*). Adsorption capacities are expressed in milligrams of CO₂ adsorbed per gram of adsorbent and *t_b* is defined as the time that the ratio of outlet C_{CO₂} to the inlet C_{CO₂} reaches 0.05. Multi-cycle adsorption/desorption performance of the adsorbents was studied to examine their durability using a temperature swing adsorption (TSA) cyclic process. For desorption, when the adsorbent was saturated, gas flow was switched to He flow and temperature was raised to 160°C and maintained at this temperature for 2 h. The adsorbents were subjected to 50 consecutive adsorption–desorption cycles and their performance was compared.

3.3 Results and discussion

3.3.1 Characterization of adsorbents

The elemental analysis, ash content, BET surface area and total pore volume of the adsorbents are summarized in Table 3-1. Elemental analysis results show that KOH activation followed by acid treatment results in an increase in the hydrogen, nitrogen and oxygen content and decrease in the carbon content of the activated carbon product. Activation conditions are selected to keep the surface area of CO₂ activated carbon and steam activated carbon in a close range in order to study the effects of activating agent and pore volume on the adsorption behavior of the samples.

Table 3-1: Physical and chemical properties of CO₂, steam and KOH activated carbons

Sample	Activation yield (%)	Elemental analysis* (wt.%)					Ash content (%)	S _{BET} (m ² /g)	total pore volume (cm ³ /g)
		C	H	N	S	O			
Steam AC	59	92.57	1.81	0.23	0.00	5.39	3.62	840	0.55
CO ₂ AC	55	92.05	2.00	0.58	0.00	5.37	4.97	820	0.45
KOH AC	35	85.98	4.29	1.21	0.01	8.51	2.02	1400	0.62

**Elemental analysis was on a dry ash-free basis, and oxygen content was determined by difference*

Figure 3-2 shows the N₂ adsorption isotherms of the activated carbon. The narrow hysteresis loops in isotherms of steam and CO₂ activated carbons indicated that both physically activated carbons were mesoporous.

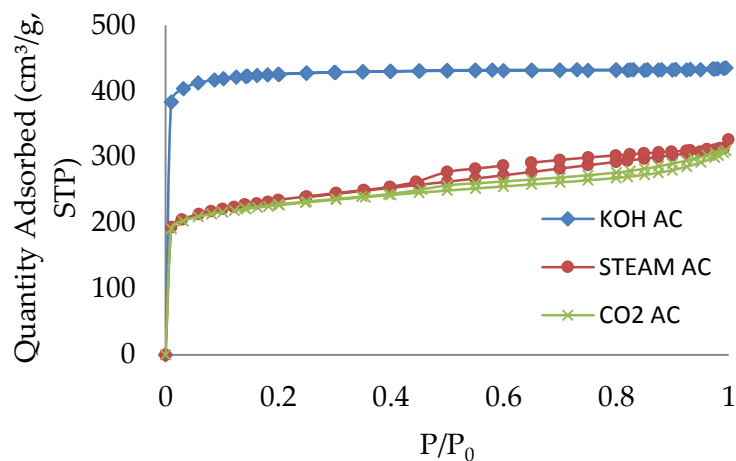


Figure 3-2: N₂ adsorption–desorption isotherms of CO₂, steam and KOH activated carbons

The micropore and mesopore size distributions of adsorbents are presented in Figure 3-3 and Figure 3-4. The ultra-micro pores, super-micropores and meso-pores ratio of samples are also shown in Figure 3-5. BET surface area of KOH activated carbon was larger than that of the physically activated carbon due to its large micropore volume. The contribution of meso-pores in chemically activated carbon porous structure was negligible. The micropore volume of steam and CO₂ activated carbon were quite close while the total pore volume of the steam activated carbon was more than that of CO₂ activated carbon. KOH activated carbon had the highest ultra-micropores and super-micropores volume.

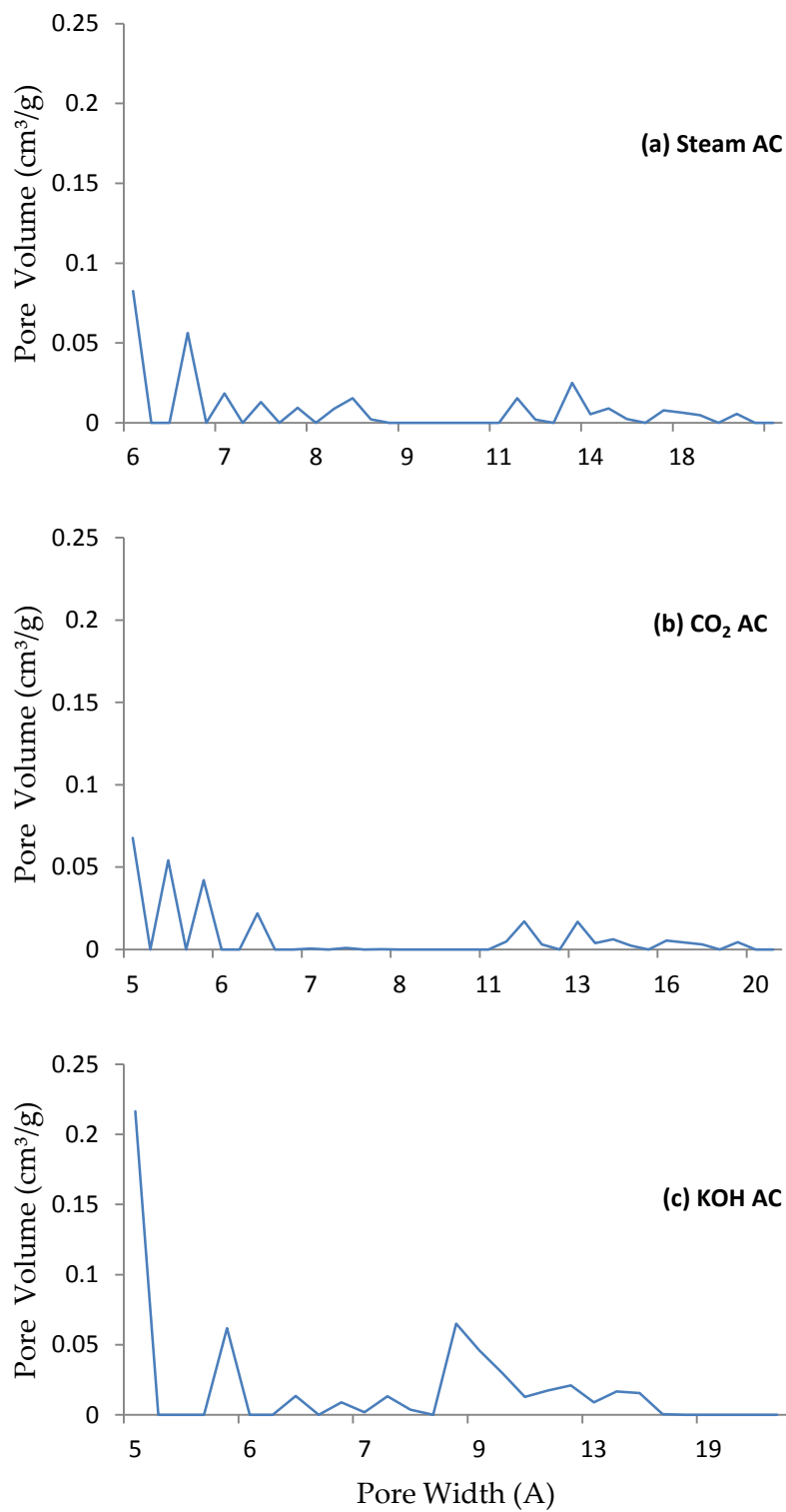
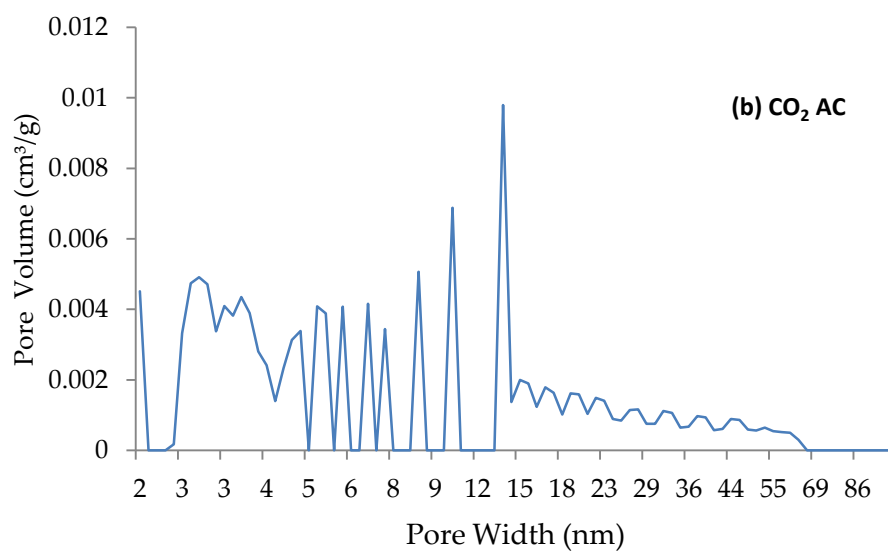
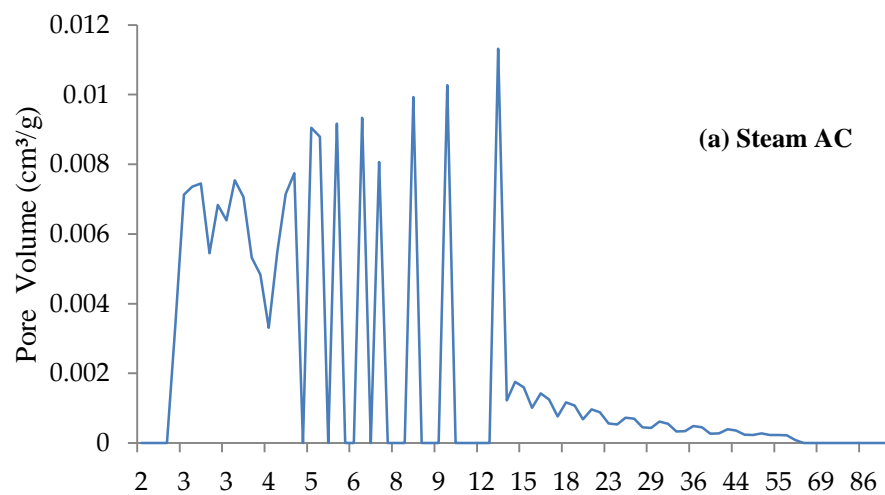


Figure 3-3: Incremental micropore volume of (a) steam, (b) CO₂ and (c) KOH activated carbons



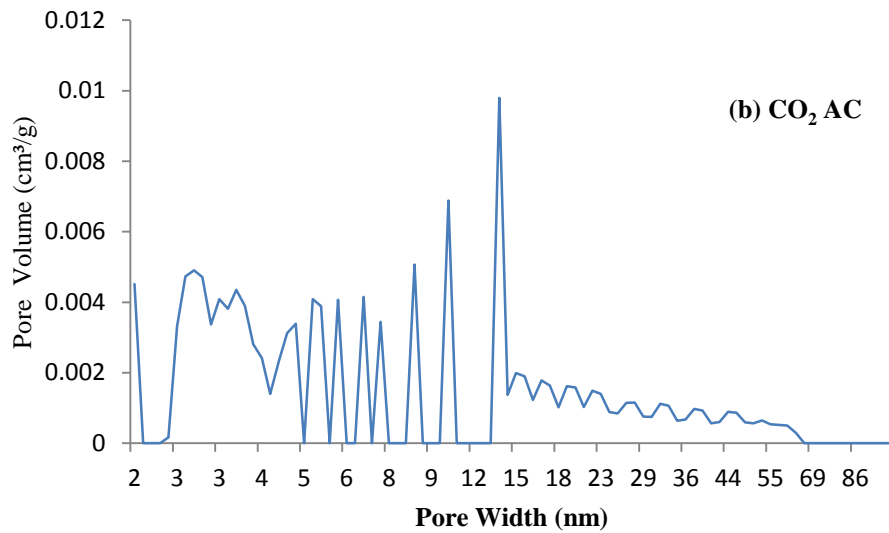


Figure 3-4: Incremental mesopore volume of (a) steam and (b) CO₂ activated carbons

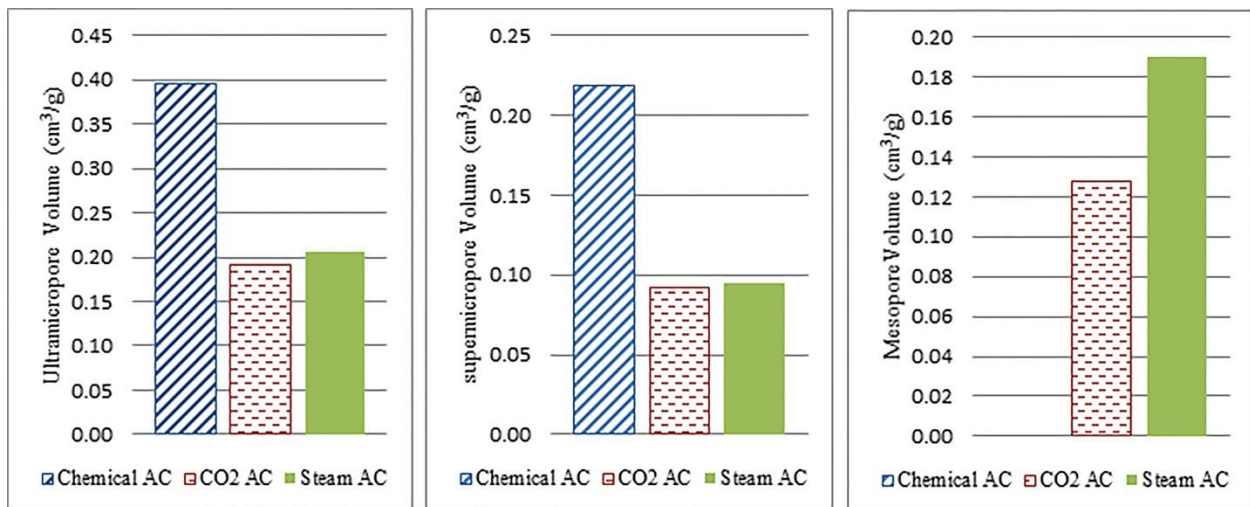
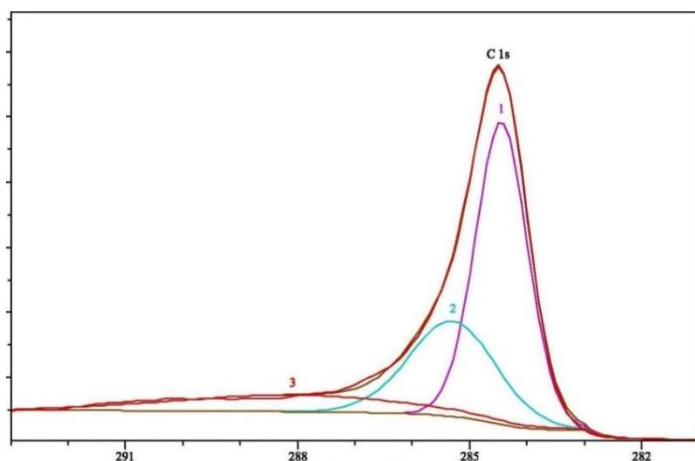


Figure 3-5: Proportion of ultra micropores, supermicropores and mesopores in KOH, CO₂ and steam activated carbons

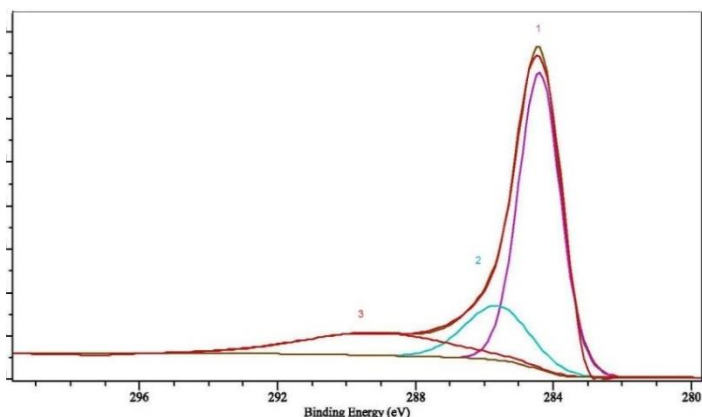
The XPS spectra and deconvolution of C1s spectra are shown in Figure 3-6, and the relative content of each functional group^{114–117} are presented in Table 3-2. The surface acidity was a result of oxygen functional groups such as phenolic, carboxyl, lactone, and aldehyde groups. Four peaks were detected in deconvolution of the C1s spectra of activated carbons: peak 1 (284.5 eV), –C=C–, graphitized carbon; peak 2 (286.1 eV), –C–OH, .C–O–C≡, C–O–R; peak 3 (288.7 eV), –C=O; and

peak 4 (289.3 eV), -COOH. Nitrogen peak was not detected on the spectra of the samples. A comparison of the C1s spectra of the different samples showed the contributions of different oxygen groups in physically and chemically activated carbons. Table 3-2 shows that the identified surface functional groups on steam and CO₂ activated carbons are similar while chemically activated carbon has a lower content of graphitic carbon and different oxygen groups on the surface. These results suggest that KOH activation process would introduce more oxygen atoms to the surface of the activated carbon. Peak 3 which represents ketone and aldehyde groups on the surface⁴⁷ was only identified in KOH activated carbon spectrum while contribution of carboxylic groups at 289.3 eV was smaller in this sample.

Steam AC



CO₂ AC



KOH AC

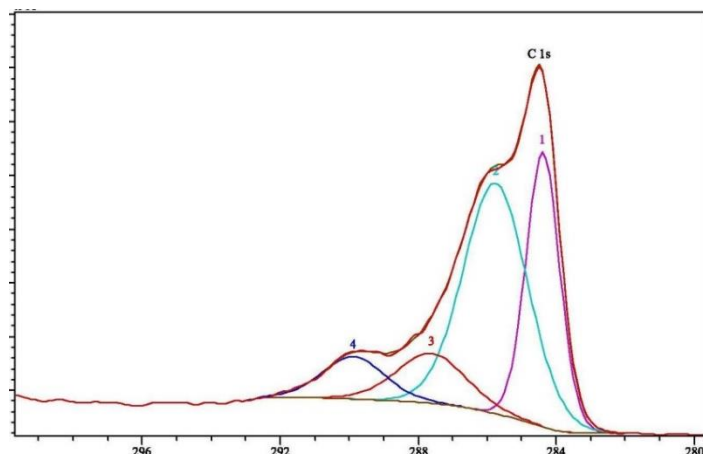


Figure 3-6: C1s XPS spectra of the activated carbons prepared using (a) steam, (b) CO₂ and (c) KOH

Table 3-2: Relative content of functional groups on CO₂, steam and KOH activated carbons based on C1s XPS spectra deconvolution

Samples	C1s (%)				
	O/C	peak 1	peak 2	peak 3	peak 4
CO ₂ AC	0.15	65.9	17.3	-	16.9
Steam AC	0.17	56.11	29.58	-	14.31
KOH AC	0.21	30.41	49.56	11.16	8.87

3.3.2 Adsorption of CO₂

The results of breakthrough adsorption measurements of KOH, CO₂ and steam activated carbons are summarized in Table 3-3. Gas adsorption begins from the bed inlet and most of the mass transfer occurs in this region. After saturation of the inlet region, the mass-transfer zone (MTZ) moves down through the bed gradually. At the t_b , the adsorbent between the inlet and the MTZ is fully saturated with CO₂. As the breakthrough continues the C_{CO_2} in the outlet increases gradually to the inlet concentration. At this point, no more adsorption can take place in the bed.

As can be seen in Table 3-3, in general, chemically activated carbon presents higher adsorption capacity than the physically activated carbon at high CO₂ concentration. This can be related to the

higher surface area and higher micropore volume specially ultra-micropore volume of the chemically activated carbon³⁰. Although according to the literature¹¹⁷, the interaction of CO₂-oxygen functional groups have negative impact on the CO₂ adsorption on the activated carbon, KOH activated carbon with higher content of oxygen groups results in a better performance which probably accounts for the larger impact of porosity of CO₂ adsorption behavior. CO₂ activated carbon and steam activated carbon present similar adsorption behavior, indicating that activating agent is not a significant parameter in CO₂ adsorption on physically activated carbons. Both temperature and C_{CO_2} affect the shape and breakthrough time of the adsorbent. As is expected, adsorption capacity of all samples decreases with increasing temperature because of the exothermic nature of CO₂ adsorption³¹ while an increase in C_{CO_2} increases CO₂ adsorption capacity dramatically. The highest and lowest adsorption capacities are achieved at 30% C_{CO_2} , 25°C and 10% C_{CO_2} , 65°C, respectively.

Table 3-3: Central composite design for two variables and corresponding adsorption capacity

Runs	Parameters		Adsorption capacity (mg _{CO₂} /g _{adsorbent})		
	Temperature (°C)	C_{CO_2} (mol.%)	KOH AC	CO ₂ AC	Steam AC
1	45.0	20	36	36	36
2	25.0	10	27	28	26
3	45.0	20	37	35	35
4	65.0	30	40	29	36
5	45.0	20	37	36	35
6	65.0	10	14	12	15
7	25.0	30	78	63	59
8	73.3	20	25	26	26
9	45.0	34.2	60	55	53
10	45.0	20	37	37	36
11	45.0	20	37	36	35
12	45.0	5.9	13	14	12
13	45.0	20	37	37	34
14	16.7	20	74.0	54	49

Figure 3-7 shows the effects of these process conditions on the breakthrough curve and t_b for all three types of adsorbents at these conditions. At 30% C_{CO_2} , 25°C, breakthrough curves of steam and CO_2 ACs coincide and chemical activated carbon presents longer breakthrough time and higher capacity but wider breakthrough curve. The wider curve can result from the mass transfer resistance or axial dispersion^{19,31} due to smaller particle size of KOH activated carbon. Results of the experiments also show that at $t > 65^\circ C$ chemical activated carbon, and consequently larger pore volume and surface area, have no real advantage over physically activated carbon. The slope of breakthrough curves and t_b also vary with temperature and C_{CO_2} .

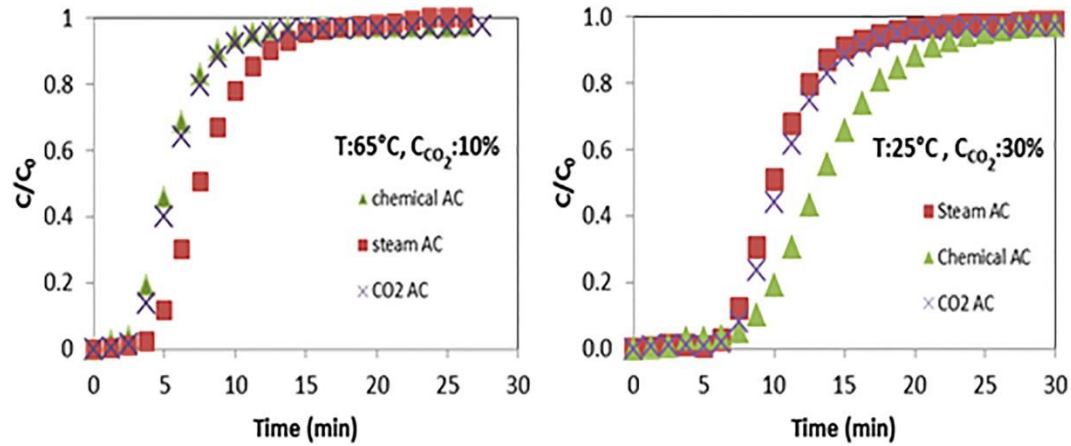


Figure 3-7: Breakthrough curves of steam, CO_2 and KOH activated carbons (ACs) performed at 65°C in 10 mol.% CO_2 in He, and at 25°C in 30 mol.% CO_2 in He

At a constant CO_2 concentration, the higher the temperature is, the narrower the mass transfer zone and the shorter t_b (Figure 3-8).

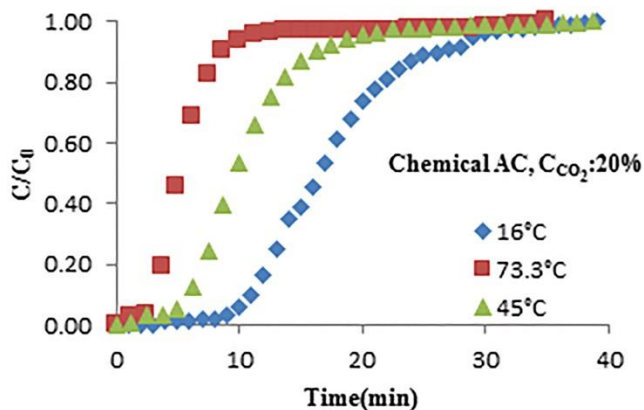


Figure 3-8: Breakthrough curves for CO₂ adsorption using KOH activated carbon performed in 20 mol. % CO₂ in He at 16, 45 and 73.3°C

On the other hand, an increase in C_{CO_2} at a constant temperature also increases the slope of the breakthrough curve, but it is less significant and it does not affect t_b (Figure 3-9).

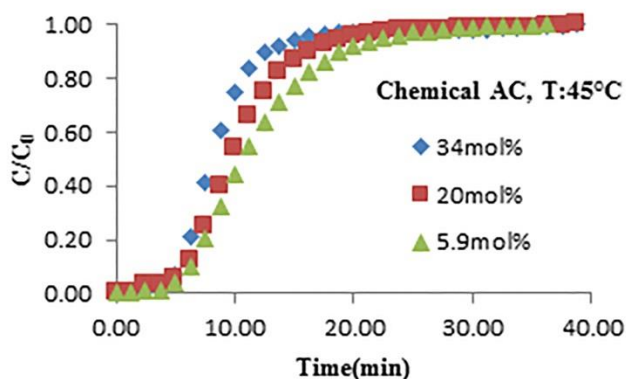


Figure 3-9: Breakthrough curves for CO₂ adsorption using KOH activated carbon performed at 45°C and 5.6 in 20 and 34 mol.% CO₂ in He

Design Expert software version 8.0.7.1 was used to analyze the results. The CO₂ adsorption results are analyzed to develop a regression model, in order to evaluate the effect of process conditions and their interactions, and to predict the adsorption behavior of adsorbent under different conditions. For the steam and chemical activated carbons, the experimental results are fitted with the quadratic models which proved the best for the lack of fit and model statistics tests. The

provisional models are tested for P -value, lack of fit and R^2 , and the final models are obtained after the elimination of the insignificant parameters and interactions. Table 3-4 presents ANOVA of CO₂ adsorption models on chemical and steam activated carbons after elimination of the insignificant terms. For CO₂ activated carbon, there is a significant lack of fit indicating that the provisional model is inadequate.

The ANOVA results for CO₂ adsorption capacity of CO₂ activated carbon are provided in Appendix C (Table C-1). For chemical activated carbon, interaction between two factors is insignificant (p -value > 0.05) and is omitted. The final model of CO₂ adsorption on chemical activated carbon as a function of temperature and C_{CO_2} is as follows (Eq. 3-2):

$$\log_{10}(\text{CO}_2 \text{ adsorption capacity}) = 1.3085 - 0.0133 T + 0.0512 C_{CO_2} + 0.0001 T^2 - 0.001 C_{CO_2}^2 \quad (3-2)$$

Eq. 3-2 shows that adsorption capacity depends directly on C_{CO_2} and the square of temperature and inversely on temperature and the square of C_{CO_2} . It also shows that C_{CO_2} has the most significant effect followed by temperature and the square of C_{CO_2} . The high value of R^2 (0.994) confirms that most of the data variation is fitted with this model. Figure 3-10a shows the response surface plot of CO₂ adsorption capacity in chemically activated carbon. For the steam activated carbon interaction of independent factors is significant (Eq. 3-3):

$$\begin{aligned} \text{CO}_2 \text{ Adsorption Capacity} = & +10.6943 - 0.3167 T + 2.6947 C_{CO_2} - 0.0150 T C_{CO_2} + 0.0022 T^2 \\ & - 0.0157 C_{CO_2}^2 \end{aligned} \quad (3-3)$$

Table 3-4: The ANOVA (Analysis of Variance) results of the response surface models for CO₂ adsorption capacity

	KOH AC				Steam AC			
	Sum of square	Mean square	df	p -value	Sum of square	Mean square	df	p -value
Model	0.67	0.17	4	<0.0001	2167.13	433.43	5	<0.0001
T	0.21	0.21	1	<0.0001	557.91	557.91	1	<0.0001
C_{CO_2}	0.42	0.42	1	<0.0001	1547.45	1547.45	1	<0.0001

TC_{CO_2}	-	-	-	-	36	36	1	0.0002
T^2	3.922E-003	3.922E-003	1	0.0236	5.79	5.79	1	0.0221
$C_{CO_2}^2$	0.037	0.037	1	<0.0001	18.26	18.26	1	0.0013
Residual	4.037E-003	5.047E-004	8		4.73	0.68	7	
Lack of fit	3.411E-003	8.527E-004	4	0.0648	2.64	0.88	3	0.3065
Pure error	6.265E-004	1.566E-004	4		2.09	0.52	4	
Total	0.68		13		2172.19		13	
R^2	0.9940				0.9978			
Adjusted R^2	0.9910				0.9963			
Predicted R^2	0.9629				0.9888			

As can be observed in Eq. 3-3, adsorption capacity of steam activated carbon increases as C_{CO_2} and the square of temperature increase and as temperature and the square of C_{CO_2} decrease but interaction of temperature and C_{CO_2} also affect the adsorption inversely. Figure 3-10b shows the three-dimensional surface response plot for CO_2 adsorption capacity of steam activated carbon as well as the effect of temperature and C_{CO_2} on CO_2 adsorption capacity.

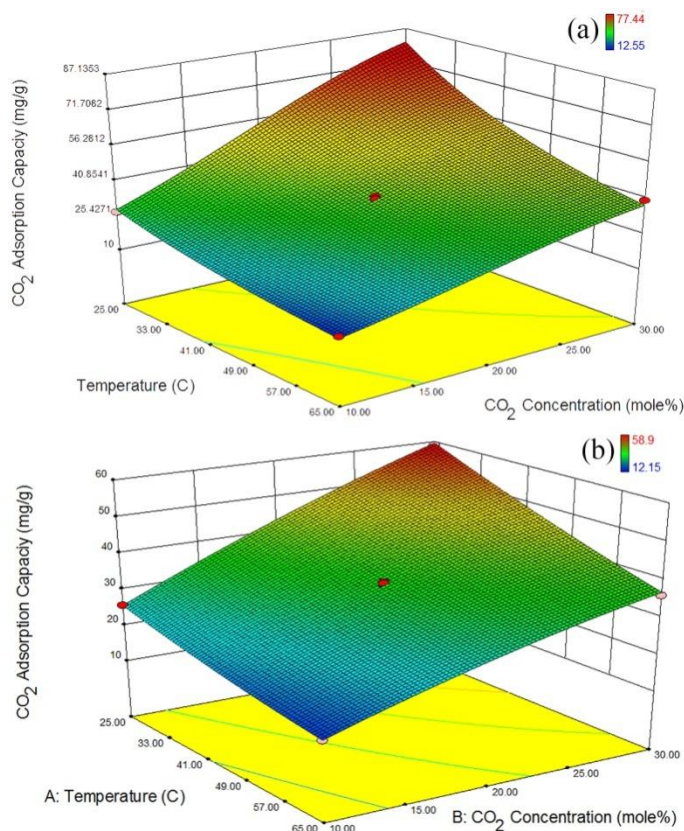


Figure 3-10: Response surface plot of CO₂ adsorption capacity of (a) KOH activated carbon and (b) steam activated carbons

3.3.3 Cyclic CO₂ adsorption

The CO₂ adsorption performance of KOH activated carbon, CO₂ activated carbon and steam activated carbon in 50 cycles is presented in Figure 3-11. The adsorption index (%) in this figure is the ratio of the adsorption capacity of the regenerated adsorbent and the fresh adsorbent¹¹⁸. As can be seen in Figure 3-11, chemical and CO₂ activated carbons can be fully regenerated and used in 50 cycles but adsorption capacity of the steam activated carbon starts decreasing after about 20 cycles, suggesting that steam activated carbon is not a favorable adsorbent for multi-cyclic CO₂ adsorption.

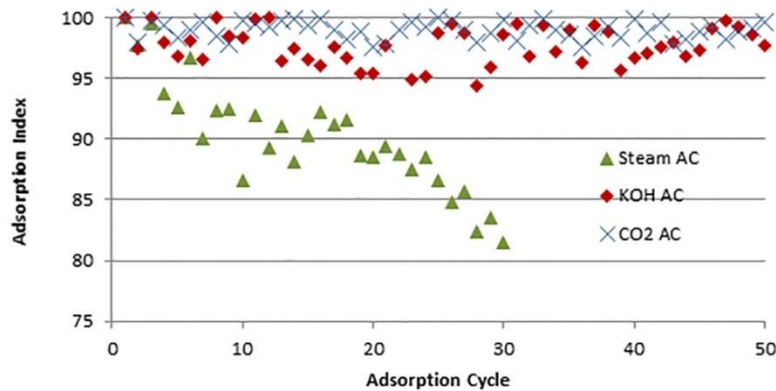


Figure 3-11: Cyclic CO₂ adsorption performed at 25 °C using steam, CO₂ and KOH activated carbons in 30 mol.% CO₂ in He

3.4 Conclusions

The CO₂ adsorption performances of KOH, CO₂ and steam activated carbons are tested under different temperatures and CO₂ concentrations. Adsorption results demonstrate that, in this range of parameters, the adsorption behavior of activated carbon can be mainly influenced by porosity of the adsorbent. Steam activated carbon and CO₂ activated carbon with the close range of surface area, the total porosity, micro porosity and similar surface chemistry present the same adsorption behavior, indicating the fact that activating agent is not a significant factor on performance of activated carbon for CO₂ capture under these operating conditions. Overall, KOH activated carbon with higher surface area and porosity can be considered as the best option for CO₂ capture at atmospheric pressure and low temperature of CO₂. It has been shown that the KOH activated carbon does not offer any advantages at higher temperature. The optimum adsorption capacity was achieved at 30% C_{CO₂}, 25°C. Moreover, all adsorbents were tested for durability and both CO₂ and KOH activated carbons remain active in a temperature swing process for at least 50 cycles and KOH activated carbon adsorbs more CO₂ under the same conditions. In this range of parameters, C_{CO₂} is also found to be the most significant factor in the adsorption process.

Chapter 4 Evaluation of the Effects of Precursors and Pyrolysis Process on Adsorption Capacity and Selectivity of Activated Carbons for CO₂ Capture

A similar version of this chapter has been published in the journal of Energy & Fuels

- *Shahkarami, S.; Dalai, A. K.; Soltan, J.; Hu, Y.; Wang, D. Selective CO₂ Capture by Activated Carbons: Evaluation of the Effects of Precursors and Pyrolysis Process. Energy & Fuels 2015, 29, 7433-7440.*

In addition, some parts of this chapter were presented at the following conferences and symposiums:

- Enhanced CO₂ Adsorption on Activated Carbon, 66th Canadian Chemical Engineering Conference, Quebec city, QC, October 16-19, 2016
- Selective CO₂ Adsorption on Activated Carbons, 24th Canadian Symposium on Catalysis Ottawa, ON, Canada, May 8-11 2016.
- CO₂ Capture on Bio-based Activated Carbons, Biorefinery I- Chemicals and Materials from thermo Chemical Biomass, Chania, Greece, September 27-October 2, 2015.
- Selective CO₂ Capture on Activated Carbon, 3rd Post Combustion Capture Conference and SaskPower Symposium, Regina, Canada, 8-11 September 2015
- Development of Activated Carbon Adsorbents for CO₂ Capture, 64rd Canadian Chemical Engineering Conference, Niagara Falls, ON, Canada, October 19-22, 2014.

Contribution of the Ph.D. candidate

In consultation with supervisors, the bench-scale adsorption set-up redesigned, installed and calibrated by Sepideh Shahkarami. All the slow pyrolysis-derived biochar samples and all the activated carbon samples were prepared by Sepideh Shahkarami. All the experiments were planned and conducted by Sepideh Shahkarami. With exception of the NEXAFS measurements, all the sample characterizations were performed and the related data were analyzed by Sepideh Shahkarami. NEXAFS measurements were carried out by Dr. Dongniu Wang at the Canadian Light Source (Saskatoon, Canada). The data analyses and interpretations were conducted by

Sepideh Shahkarami. All of the written text was prepared by Sepideh Shahkarami and all the experiments were discussed with Drs. Y. Hu, A.K. Dalai and J. Soltan.

Contribution of this chapter to the overall study

In Chapter 4, the importance of the biomass and pyrolysis techniques was discussed. The nature of the precursors and carbonization methods are also important factors in porosity and formation of the surface functional groups on the surface of the produced activated carbons. To develop an activated carbon adsorbent with tailored properties, the effects of the precursor and carbonization techniques on CO₂ adsorption capacity and selectivity of activated carbons were studied. In this chapter, the impacts of the selected biomass (precursors) and pyrolysis conditions (fast and slow pyrolysis) on the textural properties and surface chemistry of the prepared activated carbon samples are discussed and the performances of the samples in CO₂/N₂ and CO₂/O₂/N₂ feed stream is evaluated.

Abstract

Activated carbons were produced from different Canadian waste biomasses including agricultural waste (wheat straw and flax straw), forest residue (saw dust and willow ring) and animal manure (poultry litter). The precursors were carbonized through the fast and slow pyrolysis processes and then activated with potassium hydroxide. A fixed-bed reactor was used for temperature swing adsorption of CO₂ in a gas mixture of N₂, O₂ and CO₂ to study the cyclic CO₂ adsorption capacity and selectivity of the produced activated carbons. The breakthrough adsorption capacity of the produced activated carbon was measured under a flue gas condition of 15 mol% of CO₂, 5 mol% of O₂ and 80% of N₂ at 25 °C and atmospheric pressure. Slow pyrolysis based activated carbon has lower surface area and total pore volume but higher adsorption capacity in the presence of N₂. Saw dust based activated carbon synthesized using slow pyrolysis process creates the highest ultramicropores volume of 0.36 cm³/g; and the highest adsorption capacity in N₂ (78.1 mg/g) but low selectivity (2.8) over O₂ because of the oxygen functional groups on the surface. Ultra micropores and surface chemistry of adsorbents are far more important than particle size, total pore volume and internal surface area of the adsorbents. All the samples fully recovered their initial adsorption capacity in each cycle (for up to

ten cycles). This work also demonstrated that adsorption capacity and selectivity of activated carbon can be controlled and optimized through choice of starting material and carbonization conditions.

4.1 Introduction

Activated carbon (AC) is one of the oldest and well known adsorbents that present a large surface area and high degree of porosity and it has been used for different pollutant removals. However, this material has proven to show a significant decrease in its CO₂ adsorption capacity at low partial pressure of CO₂ in flue gas and in the presence of other components. The flue gas of a coal-fired power plant usually contains 14%-15% of CO₂ which is balanced with N₂, O₂ and other minor components such as CO, SO₂, SO₃ and NO_x^{26,119}. In this work, the CO₂ capture capacity, the breakthrough time and selectivity of the adsorbents for CO₂ separation in a CO₂/O₂/N₂ gas mixture of constant composition (15/5/80 mol %) was studied and compared using a fixed-bed reactor at 25 °C and 1 atmosphere.

The activated carbon preparation involves two steps of carbonization and activation⁶⁸. Carbonization is a high temperature process under inert atmosphere, which leads to elimination of most non-carbon elements. The product of carbonization, char, is then activated with an activating agent, mostly steam, CO₂, KOH or H₃PO₄¹²⁰ to develop a porous structure with large internal surface area. The heteroatoms in the produced activated carbon structure are resulted from the precursors or are associated with carbon atom during the process of carbonization and activation. The comparison of biochars derived from different sources¹² indicated that the precursors and the combustion techniques affect the chemistry of the produced biochar. Therefore, the preparation of activated carbons from different starting materials, carbonization conditions, activating agents and activating conditions can affect both physical and chemical characteristics of the final product which affect adsorption behavior of these adsorbents^{54,121}. However, the simultaneous effect of carbonization techniques and precursors on CO₂ adsorption behavior of activated carbon in simulated flue gas conditions has not been reported yet. The main purpose of this research was to study the effect of nature of precursors and carbonization process on physical and chemical properties of activated carbon and influence of these factors on CO₂ adsorption capacity, selectivity and stability of the produced activated carbon in multi-cycle

adsorption process. In the present work, three types of abundant feedstocks were used: forest residue, agricultural residue and animal manure. The selected precursors were carbonized using both fast and slow pyrolysis processes and were converted to KOH activated carbon. The physical and chemical properties of the produced activated carbon were determined by measuring BET surface area, total and micro pore volume, particle size distribution, elemental analysis, scanning electron microscope (SEM) analysis and near edge X-ray absorption fine structure spectroscopy (NEXAFS).

4.2 Material and method

4.2.1 Biomass

Three different types of waste biomass (collected in Saskatchewan, Canada) were used as precursors in this study. Pinewood saw dust (SD) and willow ring (WR) as the forest residues, wheat straw (WS) and flax straw (FS) as the agricultural residues and poultry litter (PL) as the animal manure were carbonized through fast and slow pyrolysis process. The physical and chemical properties of the flax straw, wheat straw, saw dust and poultry litter are presented elsewhere¹²². The ash content, moisture content, volatile material and fixed carbon of willow ring is provided in the Appendix D.

4.2.2 Fast pyrolysis

Fast pyrolysis of the precursors was carried out at the Saskatchewan Research Council (Saskatoon, Canada) in a mobile pyrolysis unit made by ABRI Tech Inc. (QC, Canada) at 475°C under atmospheric condition. Steel beads were used as heat carrier without any fluidizing gas. The residence time of vapor and produced char are 1 s and 15 min, respectively. The separation of char from steel beads was based on density difference. Details of the experimental set-up and properties of the produced chars are presented elsewhere¹²².

4.2.3 Slow pyrolysis

Slow pyrolysis of the biomass was performed in a one inch diameter fixed-bed Inconel tubular reactor under N₂ flow of 100 standard milliliter per minute (SmL/min) at 500 °C. The bed heating was provided using a vertical furnace and a temperature controller (Eurotherm 2416). In

each batch, 10 g of biomass was loaded in the reactor and heated to 500 °C with a heating rate of 7 °C/min. N₂ flow rate was controlled by a mass-flow controller (Brooks Instrument 5850S/B) at 100 ml/min. Temperature calibration of furnace is provided in Appendix D.

4.2.4 KOH activated carbon

10 g of produced biochar was impregnated with KOH as described in section 3.2.3 (chemical activated carbon). The produced activated carbons are denoted as follows: SD= saw dust, PL=poultry litter, WR=willow ring, WS=wheat straw, FS= flax straw, SP= slow pyrolysis and FP=fast pyrolysis. For example, activated carbon prepared from fast pyrolysis of saw dust is denoted as SD-FP AC. Figure 4-2 shows the yields of activation process. The yield of activation process is defined as the mass ratio of activated carbon to the biochar on a scale of 100⁵⁹.

4.2.5 Characterization

Elemental analysis, ash content, BET surface area, pore size distribution and total pore volume

The elemental, ash content, BET surface area, total pore volume and pore size distribution of the activated carbons were determined as described in section 3.2.4.

Particle size analysis

Particle size distribution (PSD) of the samples was determined using a laser diffraction particle size distribution analyzer (Malvern instruments Ltd., Malvern, UK). laser diffraction depends on the relationship between particle size, the angle and intensity of scattered beam. In this machine, intensity of light scattered at different angles are measured as a laser beam passes through the sample. Intensity of the scattered beam is inversely related to the particle size. Mie Scattering Theory is used to convert scattered light intensity and scattering angle into particle size information.

Scanning Electron Microscope (SEM)

The morphology and pore structure of produced activated carbons are examined by means of a field emission scanning electron microscope (SU8010, Hitachi, Japan). Scanning is performed at magnification range of 1500 to 150,000.

C 1s Near Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS)

NEXAFS is a powerful and element-specific technique which can give a better understanding of the chemical characteristics of activated carbon. Total electron yield (TEY) method was used as the detection method to collect the sample drain current (I) and normalize it by recording the beam current from a gold mesh (I_0). The powder sample was grounded and mounted on a carbon free indium foil. The High Resolution Spherical Grating Monochromator (SGM) beamline was configured for a resolving power of ca. 7500 at the C K edge (exit slit gap 50 μm) and the photon energy was scanned from 270 to 310 eV¹²³. C K-edge (1s) NEXAFS spectra were obtained on the SGM beamline 11ID-1 at the Canadian Light Source (Saskatoon, Canada). The details of sample measurements are described elsewhere¹²⁴.

4.2.6 Breakthrough CO₂ adsorption measurements

All the experimental breakthrough curves were obtained by passing the gas mixture through the one-inch fixed-bed Inconel tubular reactor. Chemical analysis was conducted using a dual channel micro-gas chromatograph (490 micro-GC, Agilent Technologies Inc., USA) equipped with a micro-thermal conductivity detector (μTCD). The inlet flow rates, outlet flow rates and CO₂/N₂/O₂ mole fractions are measured using mass flow controllers, flow meter and micro-GC, respectively, for breakthrough adsorption. All the breakthrough experiments were repeated twice, and the average values were reported. Argon and helium are used as carrier gases in the dual channel micro-gas, respectively. Channel one column separates and measures nitrogen and oxygen while channel two column separates and analyzes carbon dioxide. The TCD is calibrated using mixtures of known composition. The GC calibration data is provided in Appendix D. schematics of experimental set-up is shown in Figure 4-1 and related calibration data are provided in Appendix D. The adsorption measurements involve two steps of measuring the CO₂ adsorption capacity in a N₂/CO₂ (85/15 mol %) feed stream and then measuring the CO₂

adsorption capacity and selectivity of CO₂ in N₂/CO₂/O₂ feed stream (80/15/5 mol %). The reactor is loaded with 1.5 g of activated carbon and pre-heated at 160 °C for 2 h under N₂ before the adsorption experiments. After cooling down to 25 °C, the feed gas is passed through the reactor. The total feed flow rate in both steps is held constant at 50 SmL/min. The adsorption process is continued until saturation where the outlet concentration of CO₂ reaches the inlet concentration of CO₂. Adsorption capacity and selectivity were calculated as described in section 2.3.1.

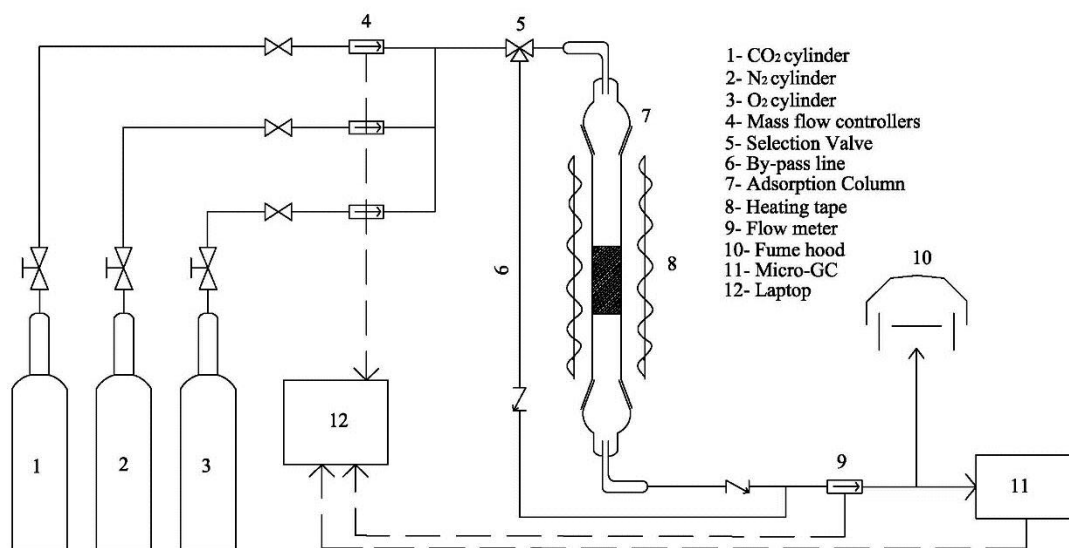


Figure 4-1: Schematic diagram of the adsorption set-up

Multi-cycles adsorption/desorption are studied for the adsorbents to examine their durability using a temperature swing adsorption (TSA) cyclic process. For desorption, when the adsorbent is saturated, gas flow is switched from feed gas to N₂ flow and temperature is raised to 160 °C for 2 h. The adsorbents are subjected to 10 continuous adsorption–desorption cycles and their performance are compared.

4.3 Results and discussions

4.3.1 Characterization of adsorbents

Figure 4-2 illustrates the effects of carbonization techniques on the yield of the produced activated carbon for each of the precursors. It is evident that slow pyrolysis generally results in

higher activation yields. The higher pyrolysis and activation yields of the slow pyrolysis products can be attributed to the secondary coking and re-polymerization reactions due to the longer vapor–solid residence time and low heating rate in the slow pyrolysis process¹²⁵. The yields of poultry litter based AC obtained through both fast and slow pyrolysis process were found to be significantly lower than others.

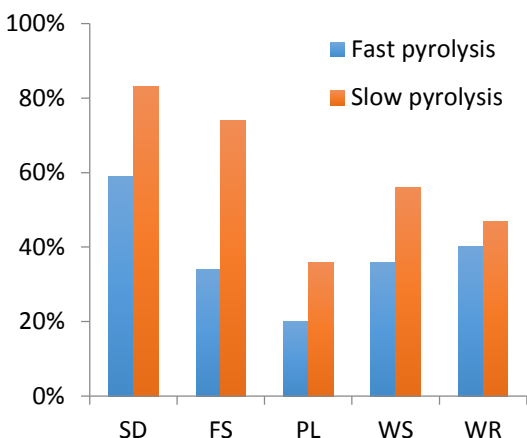


Figure 4-2: Yield of saw dust, flax straw, poultry litter, wheat straw and willow ring based activated carbons

The particle size distributions of the produced activated carbons from the precursors in both slow and fast pyrolysis are shown in Figure 4-3. Samples derived from saw dust comprise smaller particles than samples derived from other precursors. As it can be observed in Figure 4-3, the FP based ACs are generally finer. In FP based ACs, SD-FP AC is the finest produced sample followed by FS-FP AC; and WR-FP AC is the largest produced sample. In SP based ACs, SD-SP AC has the finest particle size distribution followed by WR-SP AC and FS-SP AC, and PL-SP AC has the largest particle size.

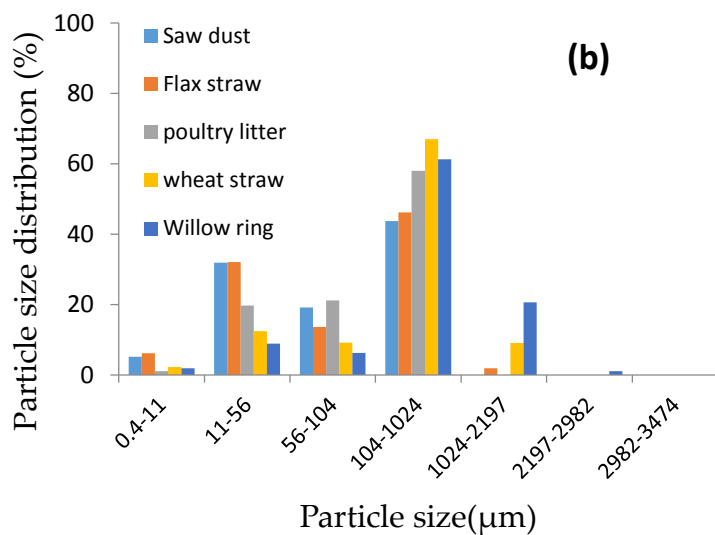
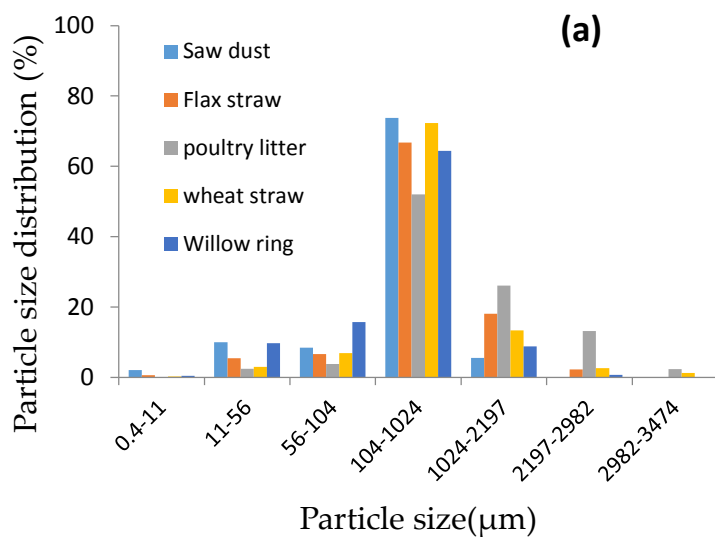


Figure 4-3: Particle size distribution of (a) slow pyrolysis based and (b) fast pyrolysis based activated carbons

The SEM images of the biochar and activated carbon are shown in Figure 4-4. As it can be observed in Figure 4-4, there are significant differences in the surface morphology of the produced activated carbon samples. PL-FP AC has a uniform and highly porous honey-comb structure. FS-FP and WS-FP ACs also exhibit a well pronounced array of honey-comb structures, indicating higher possibility of gas trap. Although the honey-comb structure cannot be seen at 12k resolution in SD-FP AC, a fully developed array of honey-comb structures is

observed at 150k (Figure 4-4k). The SEM images of SP based ACs had an irregular and porous surface. It demonstrates that there are small cavities and attached fine particles on the SP activated carbon surface.

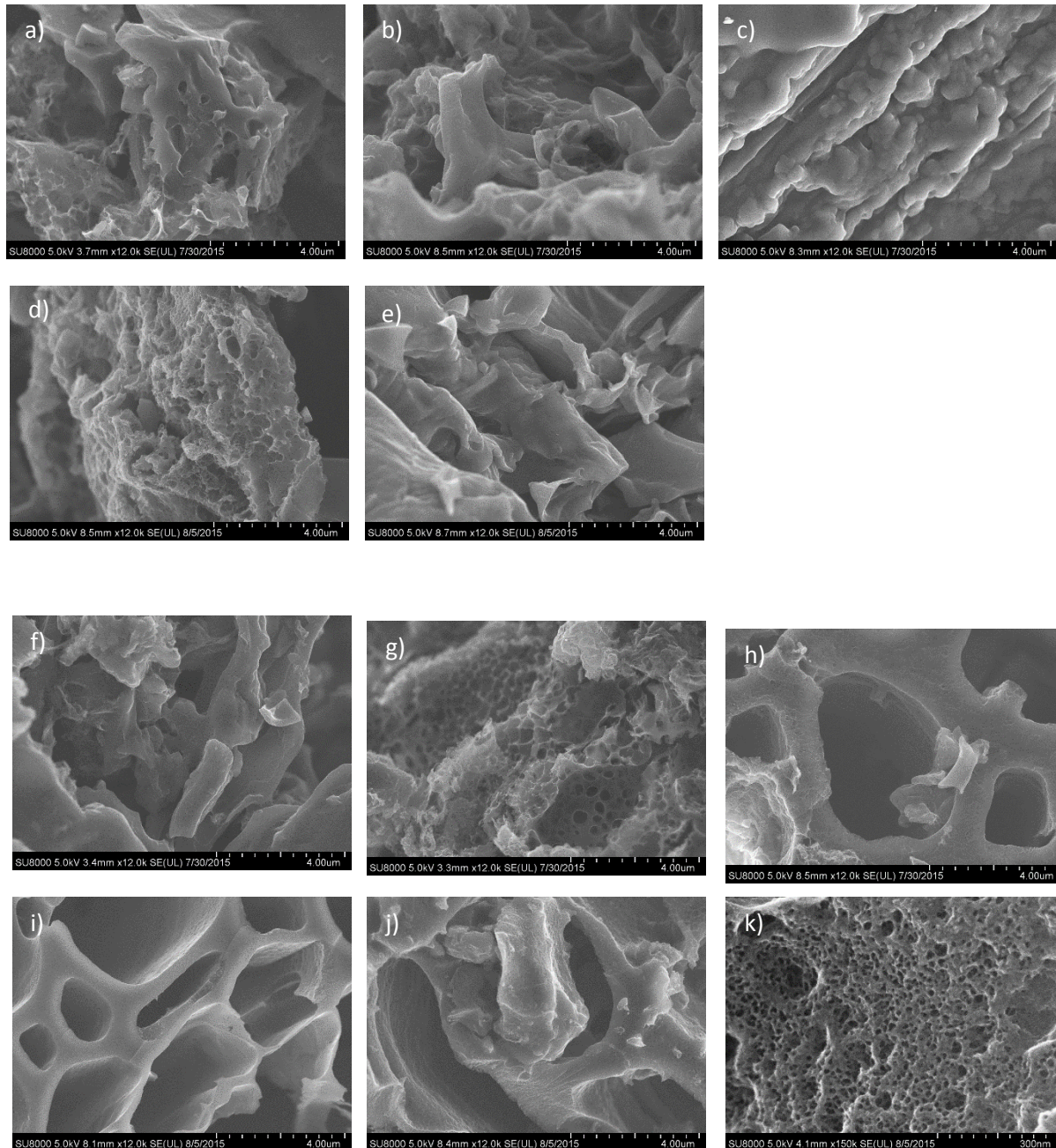


Figure 4-4: SEM images of a) willow ring-slow pyrolysis, b) poultry litter- slow pyrolysis, c) flax straw-slow pyrolysis, d) wheat straw- slow pyrolysis, e) saw dust- slow pyrolysis, f) willow ring-fast pyrolysis, g) poultry litter- fast pyrolysis, h) flax straw- fast pyrolysis, i) wheat straw- fast pyrolysis, j) saw dust- fast pyrolysis activated carbon (12K magnification) and k) SD-FP activated carbon (150K magnification)

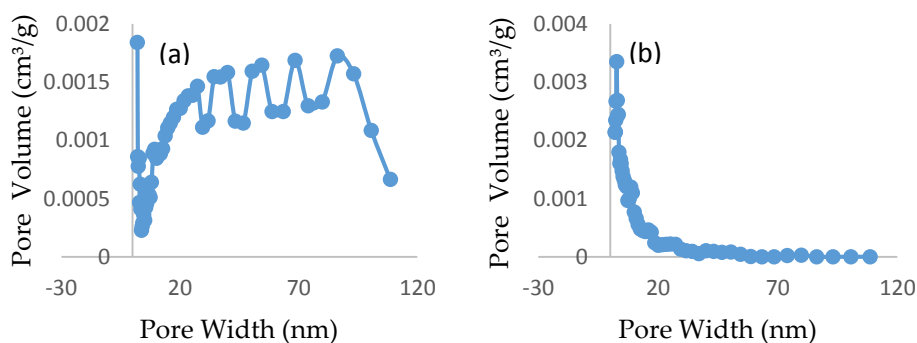
The characteristics of activated carbon samples are presented in Table 4-1. The reported elemental analysis is on dry ash-free basis. Ash in the activated carbons is the inorganic residuals of the precursors. Ash contents of the PL-FP and PL-SP ACs are 1.12% and 0.54%, respectively, which are much lower than those of biochar samples¹²². The small amount of ash content and low activation yield of PL based AC suggest that most of the ash content is eliminated through the acid treatment process¹¹⁰ which results in production of fine powders with high carbon content and extended surface area.

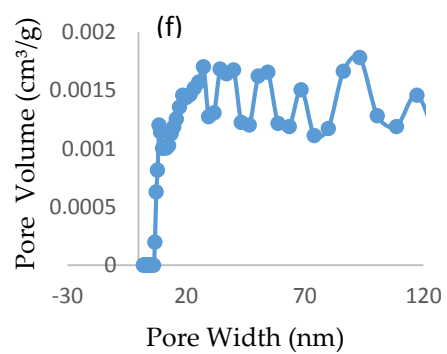
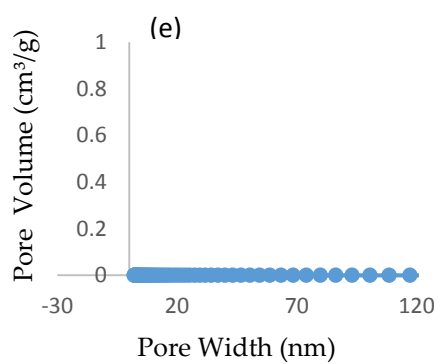
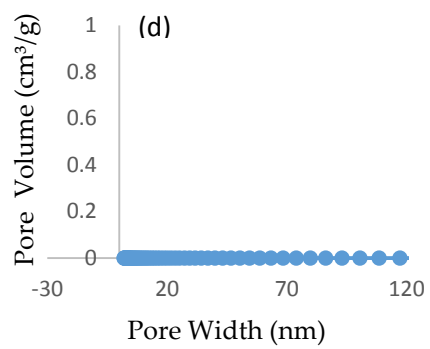
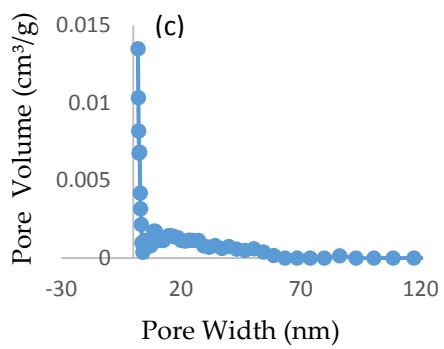
Table 4-1: Elemental analysis and physical properties of produced activated carbons

	Fast Pyrolysis					Slow Pyrolysis				
	SD-FP	FS-FP	PL-FP	WS-FP	WR-FP	SD-SP	FS-SP	PL-SP	WS-SP	WR-SP
N, wt%	0.43	1.43	0.90	0.58	0.48	0.20	0.44	0.58	0.30	0.44
C, wt%	89.58	85.54	86.46	84.13	86.21	88.13	85.37	90.52	82.59	84.89
S, wt%	0.02	0.03	0.13	0.04	0.10	0.03	0.15	0.04	0.04	0.02
H, wt%	2.33	2.63	2.61	2.55	2.25	2.74	3.61	2.25	3.16	2.69
O, wt% (by difference)	7.64	10.37	9.90	12.70	10.96	8.91	10.42	6.61	13.90	11.96
Ash content, wt%	0.79	1.21	1.12	2.37	2.52	0.72	0.84	0.54	4.86	2.49
BET, m ² /g	1501	1660	2889	1462	1602	1268	1281	1879	1212	1563
Ultra Micropore volume, cm ³ /g	0.224	0.151	0.101	0.149	0.192	0.360	0.252	0.063	0.243	0.313
Micropore volume, cm ³ /g	0.527	0.577	1.017	0.476	0.589	0.430	0.453	0.616	0.406	0.574
Mesopore volume cm ³ /g	0.044	0.038	0.162	0.044	0.038	0.000	0.000	0.046	0.042	0.034

Macropore	0.009	0.00	0.035	0.091	0.014	0.00	0.00	0.03	0.00	0.01
volume cm ³ /g		1				0	0	2	0	7
Total pore		0.83				0.43	0.45	0.69	0.44	0.62
volume, cm ³ /g	0.580	7	1.214	0.612	0.641	0	3	4	8	5

Elemental analysis results show that fast pyrolysis followed by KOH activation, compared to slow pyrolysis process, results in an increase in nitrogen content and decrease in hydrogen content of the produced activated carbons. The types of the precursor and pyrolysis conditions also influence surface areas and porosity characteristics of the produced activated carbons. The pore size distributions of the produced activated carbon are provided in Figures 4-5 and 4-6. The activated carbons produced through fast pyrolysis have larger surface area, total pore volume and total micropore volume while the contribution of ultra-micropores is lower in these samples. Moreover, the contribution of mesopores in FP based AC is more significant. In both cases, PL based AC shows the largest surface area, largest total pore volume and smallest ultra-micropores volume.





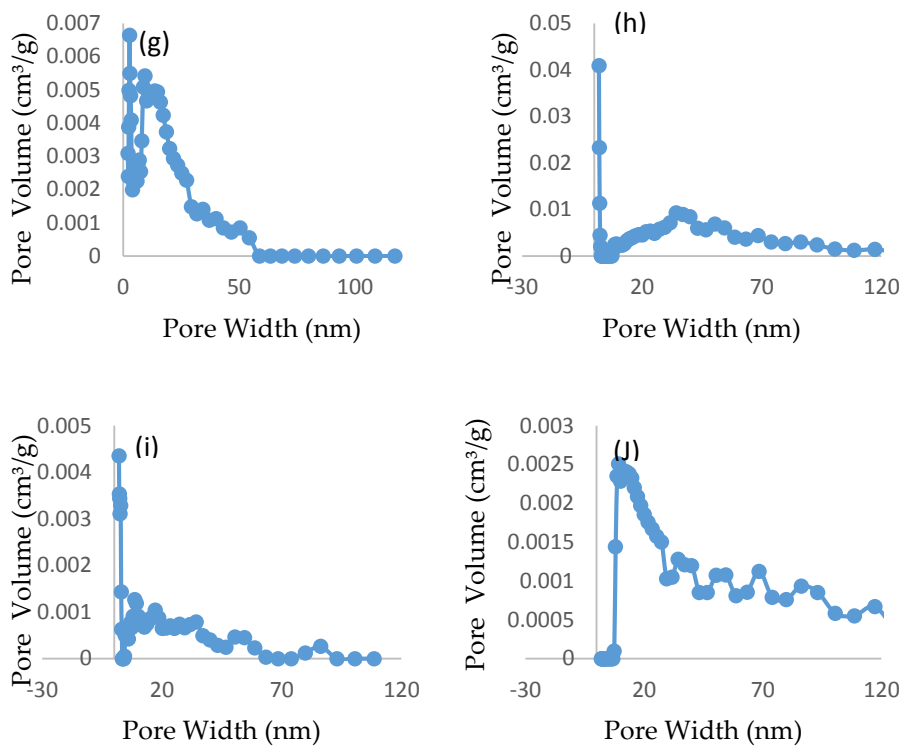
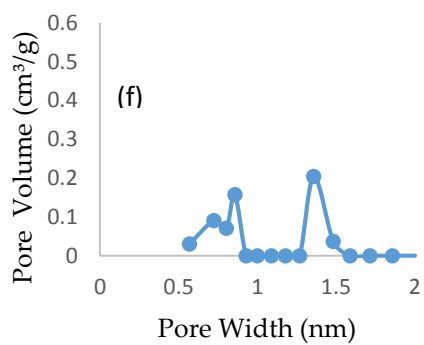
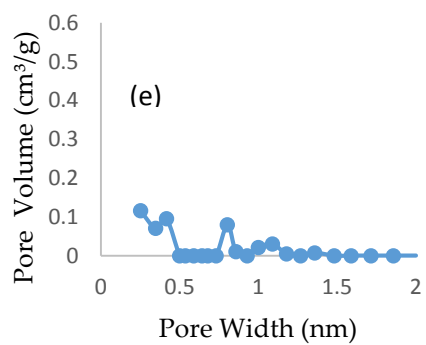
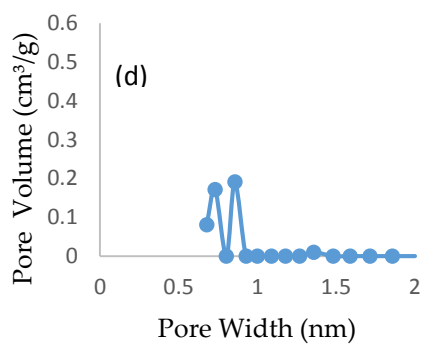
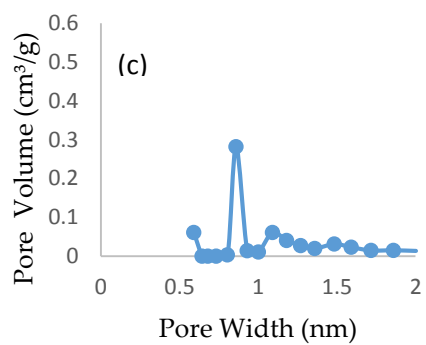
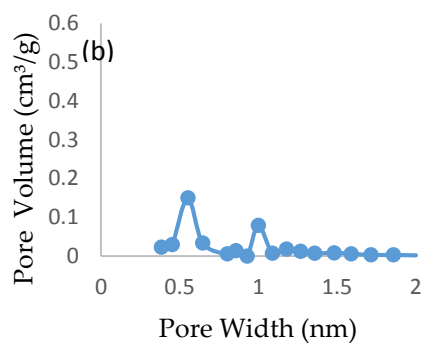
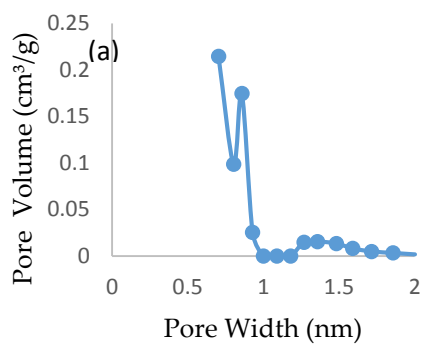


Figure 4-5: Incremental mesopore and macropore volume of (a) WR-SP, (b) WS-SP, (c) PL-SP, (d) FS-SP, (e) SD-SP, (f) WR-FP, (g) WS-FP, (h) PL-FP, (i) FS-FP and (j) SD-FP



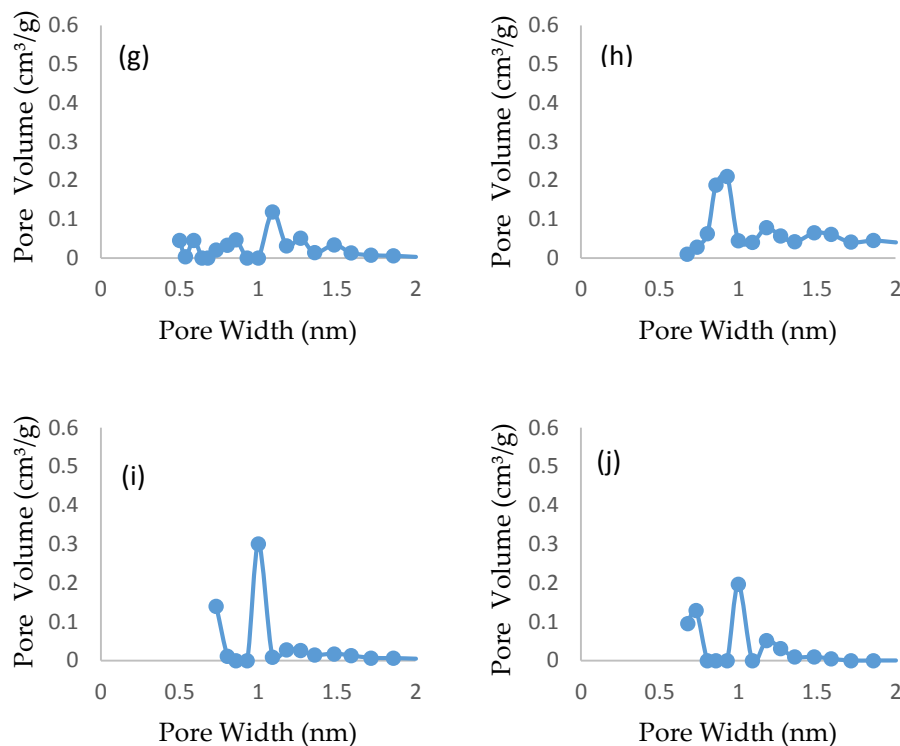


Figure 4-6: Incremental micropore volume of (a) WR-SP, (b) WS-SP, (c) PL-SP, (d) FS-SP, (e) SD-SP, (f) WR-FP, (g) WS-FP, (h) PL-FP, (i) FS-FP and (j) SD-FP

The C K-edge NEXAFS spectra of SP based ACs are compared in Figure 4-7(a). Three region are common in the C K-edge spectra appearing at 285 eV (C=C), 288 (C/O) and 292 eV (δ^*). In all the samples, two $C1s \rightarrow \pi^*$ transitions near 285.4 eV and 288.4 eV are dominant. However, the aromaticity is the main feature of the spectra exhibiting as an asymmetric peak transition near 285.4 eV in all the spectra of the SP based ACs with the exception of SD-SP AC. This peak is correlated with $C1s - \pi^*$ transition of aromatic (C-R) or double-bonded alkyl carbon (C=C)^{123,126}. The symmetry and broad of this peak suggest multiple resonance¹²³ in this region. The small shoulder near 284.5 eV is attributed to the $C1s - \pi^*$ transition of unsaturated C=C^{127,128} which is more notable in FS-SP and WR-SP ACs. In SD-SP AC, the intensity of 285.2 eV peak is remarkably smaller followed by a broad shoulder at 287.2 eV and a sharp peak at 288.4 eV (Figure 4-7 (a)). The $C1s \rightarrow \pi^*_{C=O}$ transition at 288.4 eV represents unsaturated carboxylic carbon^{123,129,130}. This distinct peak at 288.4 eV also indicates that SD-SP AC has considerably

more $C=O \pi^*$ bonds in its structure compared to other SP based ACs. The broad shoulder centered at 287.2 eV reveals overlapping bonds in this region that present different functional groups on the surface. This transition corresponds to C-O bond and the aromatic carbons with oxygen substitute including phenolic, ether or a ketone groups^{123,129,131,132}. In addition, the spectrum of PL-SP AC exhibits a shoulder at 285.8 eV. The shoulder near 284.3 eV is inconspicuous. However, an additional shoulder appeared as a peak at 285.74 eV. Since the change in the polarization of electron cloud in a chemical bond leads to energy shifts in the transition¹²³, this shoulder can be correlated to the bonding of a substituent to the benzene ring results^{133,134}. The intensity of the transition at 288.4 eV is also much weaker in PL-SP AC reflecting the lower carboxyl content in this sample. Finally, the spectra of FS-SP, WR-SP and WS-SP ACs are very similar. However, the peak intensities at 285.42 eV and 288.4 eV in FS-SP spectrum are considerably smaller due to the fewer $C=C \pi^*$ and $C=O \pi^*$ bonds in FS-SP AC, respectively¹²⁶. The spectra of WS-SP AC revealed a peak centered at 287.1 eV reflecting a small portion of phenolic, ether or ketone groups in its structure. The peak near 289.5 eV is also observed in all the spectra reflecting the transition O-substituted alkyl carbon groups such as alcohol groups or carbonyl groups^{123,129,130}. The SD-SP and PL-SP ACs present unique characteristics in their spectra suggesting differences in the functional groups distributions and surface properties. SD-SP AC exhibits a small portion of aromatic $C1s \rightarrow \pi_{C=C}^*$ and the largest proportion of $C1s \rightarrow \pi_{C=O}^*$ transition in its spectra which is similar to that of marine sediments¹²³ while soot, grass char and wood char¹²³ exhibit a higher proportion of $C=C \pi^*$ in their spectra. On the other hand, PL-SP AC spectra reveal a pronounced peak of $C1s \rightarrow \pi_{C=C}^*$ transition and the carboxylic peak is significantly smaller.

The C K-edge NEXAFS spectra of FP based ACs are shown in Figure 4-7(b). In FP samples, two transitions near 285.4 eV and 288.4 eV are common to all of the FP spectra with the exception of SD-FP AC. The shoulder of unsaturated C near 284.2 eV is more distinct in the FP based ACs. SD-FP AC shows a significantly different spectrum from the other fast pyrolysis products, exhibiting a broad and intense peak at 284.4 eV followed by a notable shoulder centered at 285.1 eV. The difference in the aromatic C peak position in the SD-FP AC is attributed to significant presence of unsaturated C in SD-FP AC. Besides, the peak of oxygenated

groups centered at 288.4 eV show a lower intensity as compared to SD-SP AC suggesting smaller amounts of C=O in its structure. The shoulder near 287 eV representing the overlapping bonds in 286-287.9 eV is observed in all the FP samples. However, this shoulder is more distinct in SP-FP and WS-FP ACs. The features of FS-FP and WR-FP AC spectra in particular are similar to PL-FP AC spectrum.

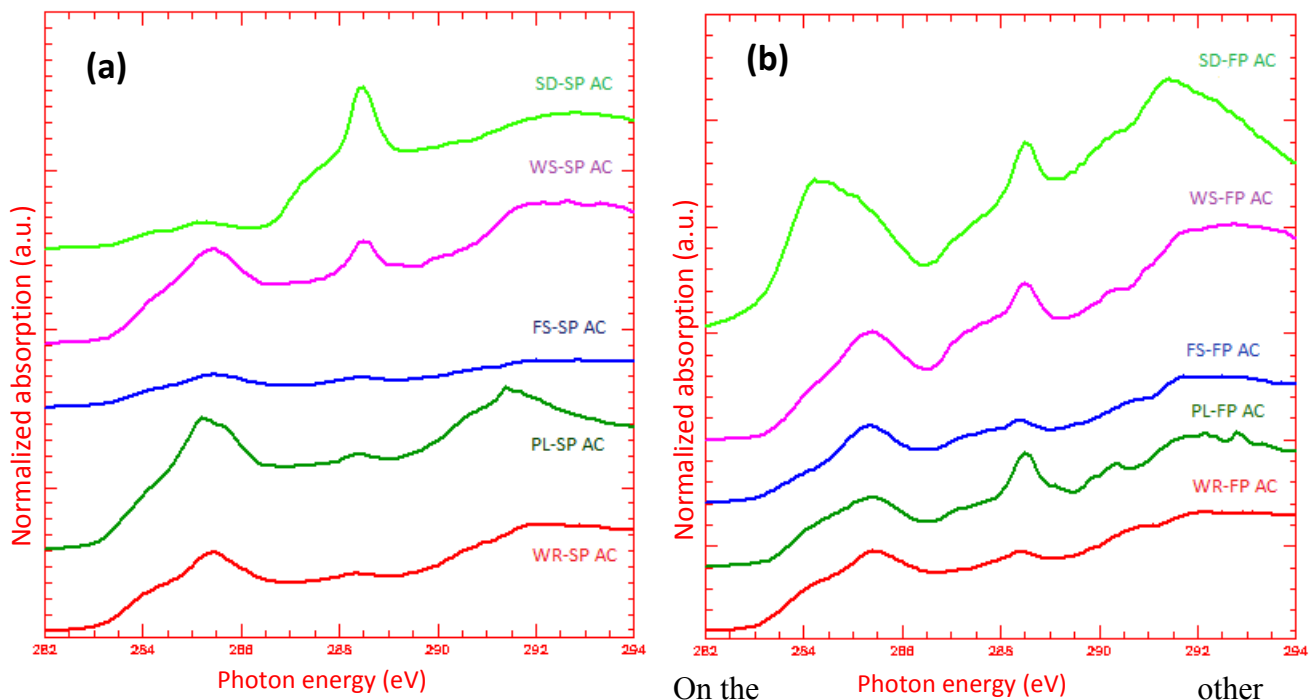


Figure 4-7: C 1s NEXAFS spectra of (a) slow pyrolysis based ACs and (b) fast pyrolysis based ACs

hand, WR-SP and WR-FP ACs reflect the same features in their spectra indicating they have similar surface properties. PL-FP AC exhibits a broad asymmetric peak at 285.3 eV with a shoulder at a lower 284.35 eV. The sharp peak at 288.5 eV reflects a much larger contribution of carboxylic group as compared to PL-SP AC. Although a distinct trend is not observed in these samples, it is obvious that there are significant variations in the degree of oxidation and functional groups in fast and slow pyrolysis. The dominant functional group for a fast pyrolysis product is carboxylic while slow pyrolysis process mostly leads to a highly aromatic structure.

4.3.2 Adsorption of CO₂

The breakthrough curves of CO₂ adsorption and the average results of cyclic breakthrough adsorption measurements in CO₂/N₂ and CO₂/O₂/N₂ gas mixtures are shown in Figure 4-8 and Table 4-2, respectively.

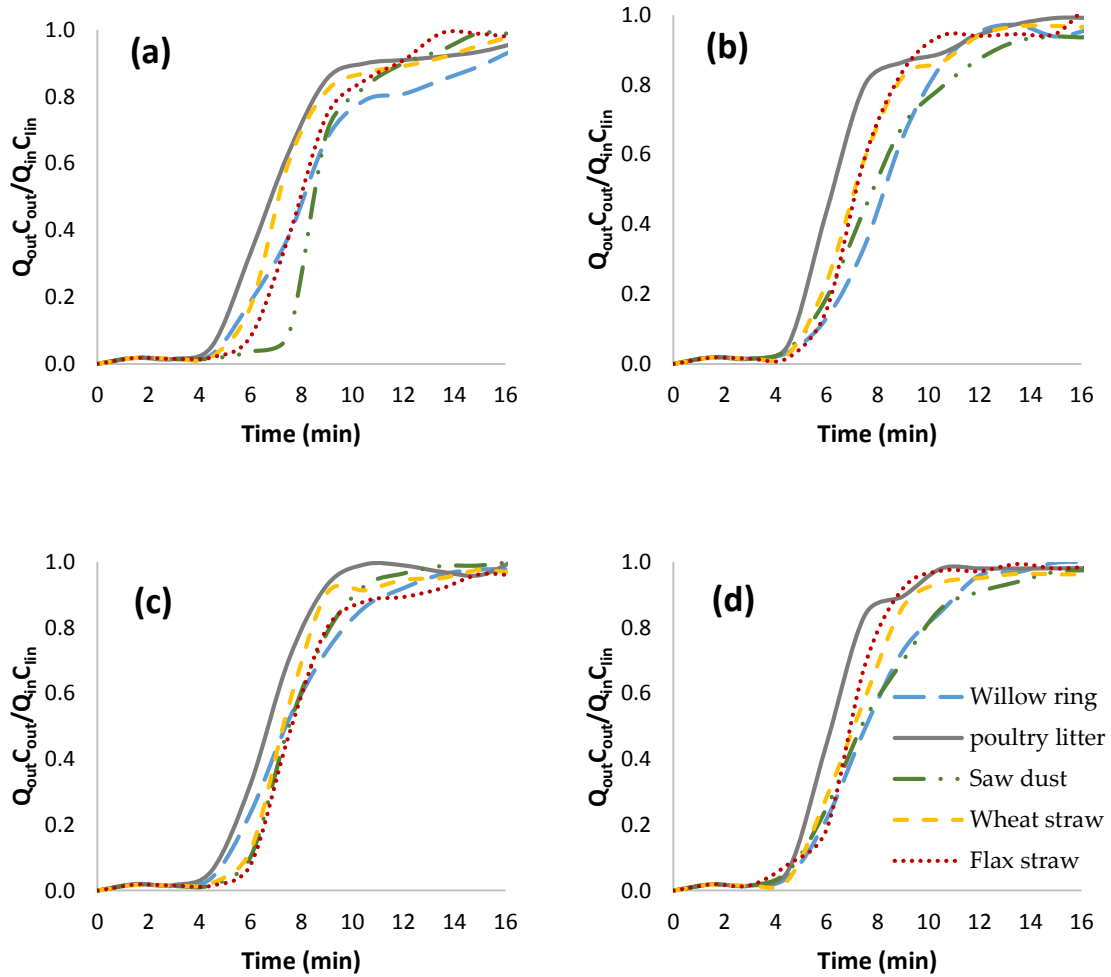


Figure 4-8: Breakthrough curves of ACs in a) slow pyrolysis samples in N₂/CO₂ feed stream b) fast pyrolysis samples in N₂/CO₂ feed stream, c) slow pyrolysis samples in N₂/CO₂/O₂ feed stream and d) fast pyrolysis samples in N₂/CO₂/O₂ feed stream

The experiments include ten consecutive cycles where the adsorbent reached saturation and then was regenerated during the TSA process. All samples adsorbed CO₂ reversibly and regained

more than 90% of their initial adsorption capacity by regeneration. The cyclic CO₂ adsorption performance of the produced activated carbon is presented in Figure 4-9.

The largest breakthrough time and adsorption capacity are found to be 7.5 min and 78.1 mg/g of SD-SP AC, respectively; and the lowest breakthrough time and adsorption capacity are for PL-FP AC (4.5 min, 55.5 mg/g) in the CO₂/N₂ gas mixture.

Table 4-2: CO₂ adsorption capacities and selectivities of the produced activated carbons from the breakthrough measurements with CO₂/N₂ and CO₂/N₂/O₂ mixtures at 25°C

	Fast Pyrolysis					Slow Pyrolysis				
	SD-FP	FS-FP	PL-FP	WS-FP	WR-FP	SD-SP	FS-SP	PL-SP	WS-SP	WR-SP
Adsorption Capacity in N ₂ , mg/g	73.6	66.0	55.5	64.3	70.3	78.1	72.2	61.7	70.8	75.1
Standard Deviation	0.28	0.04	0.85	0.42	0.11	0.42	0.42	0.91	0.28	0.07
Adsorption Capacity in N ₂ & O ₂ , mg/g	69.5	60.2	54.8	62.7	67.2	65.9	66.5	60.9	70.5	70.1
Standard Deviation.	0.83	0.42	0.63	0.77	0.42	0.28	0.14	0.83	0.98	0.28
Selectivity over O ₂	3.9	2.6	2.1	2.7	2.7	2.8	2.9	2.8	3.5	3.2
Selectivity over N ₂	28.1	22.3	17.4	22.1	25.8	29.3	27.9	22.0	26.0	28.6

This steep curve results in maximizing adsorbent capacity at the breakpoint. As shown in Table 4-2, in spite of their smaller surface area and smaller pore volume, SP based ACs have larger adsorption capacity than the FP based ACs in CO₂/N₂ feed mainly due to their higher ultra-micropore volume reflecting that the ultra-micropores is a selective factor for CO₂ adsorption in CO₂/N₂ mixture. Similar results have also been reported before^{30,135–137} suggesting that the overlap of potential fields of opposite pore walls enhances the interaction of CO₂ molecules and pore walls in the pore width <1nm^{30,138}. These results indicate the important role of ultra-micropores in CO₂ adsorption as compared to surface area and total pore volume. In addition, Liu et al.²⁰ showed that CO₂ is selectively adsorbed on the adsorbents with oxygen functional groups on their surfaces due to the strong quadrupole moment of CO₂ compared to that of N₂. In both cases, in CO₂/N₂ feed stream, SD based ACs present the highest adsorption capacity and selectivity followed by WR-SP AC while PL based ACs exhibit the lowest adsorption capacity. This substantiates the important effect of nature of the precursors on adsorption behavior of activated carbon. When multicomponent adsorbates are contained in the feed, breakthrough behavior becomes more complicated¹³⁹. To study the effects of presence of oxygen in feed stream on adsorption behavior of the samples, the CO₂/N₂/O₂ breakthrough curves are compared to CO₂/N₂ results. Because N₂, CO₂, and O₂ have kinetic diameters of 3.64, 3.30, and 3.46 °A¹⁹, respectively, separation of O₂ and CO₂ is more difficult. Both are nonpolar and have similar kinetic diameters, therefore the adsorbent cannot differentiate CO₂, and O₂. In all cases, a reduction of the t_b and adsorption capacity is observed in the presence of oxygen in feed which suggests that O₂ is a stronger adsorbate⁴⁵ than CO₂ to adsorb on activated carbon. This could be caused by the differences in the molecular weight of O₂ and CO₂ which facilitates the O₂ diffusion in the bulk gas. For SP based ACs, the most and least selective CO₂ adsorptions occur on WS-SP and SD-SP AC, respectively. While for FP based ACs, SD-FP and PL-FP are the most and least selective adsorbent which can be attributed to the oxygen functional groups on the surface of adsorbents. SD-SP AC with highest content of oxygen functional groups appeared to be the least selective for CO₂ while SD-FP with a small content of C=O bonds in its structure and a much larger contribution of C=C is highly selective for CO₂ over N₂. The impact of surface chemistry is obvious by observing the trend of selectivity in Table 4-2 which confirms that although the presence of ultra micropores is the dominant factor for CO₂ adsorption on activated carbon, the oxygen functional groups on the surface can also significantly affect the adsorption

selectivity. The results also show that pyrolysis conditions affect the breakthrough curve of the adsorbents. A comparison between the SD-FP AC and SD-SP AC in Figure 7 shows a sharper breakthrough curve due to the higher mass transfer rate of the SD-SP AC in CO₂/N₂ mixture. Since molecular diffusivity in a multicomponent mixture is a function of mole fraction of species and molecular weight, the presence of oxygen results in a wider breakthrough curve in CO₂/O₂/N₂ mixture¹⁴⁰.

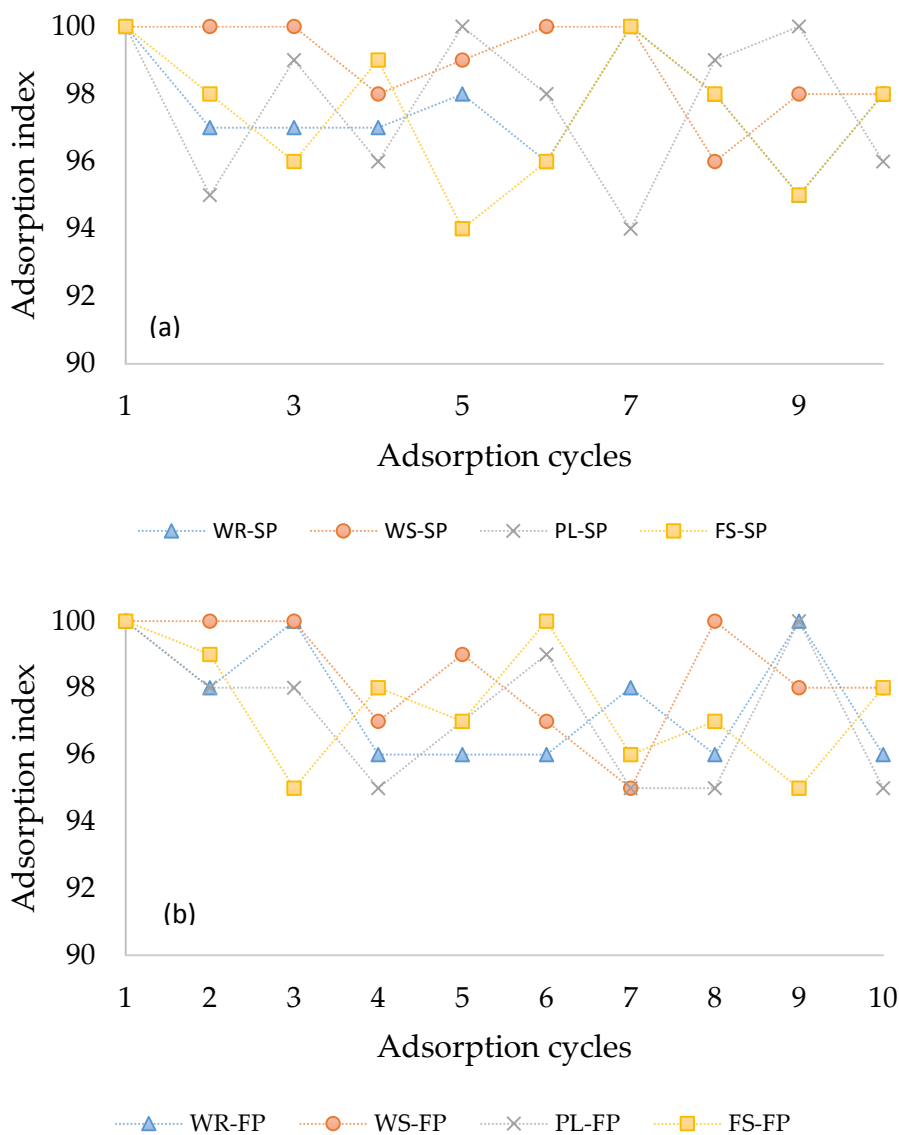


Figure 4-9: The cyclic CO₂ adsorption performance of (a) slow pyrolysis activated carbons and (b) fast pyrolysis activated carbons in CO₂/N₂

4.4 Conclusions

The major differences in surface chemistry, porous structure and morphology of activated carbons derived from the fast and slow pyrolysis of different source of biomass are identified. Overall for the same precursor, the fast pyrolysis process leads to larger surface area and total pore volume, smaller particle size and ultra-pore volume, and a larger contribution of phenolic/ketone and carboxylic groups. A slow pyrolysis process leads to formation of extensive aromatic regions with smaller contribution of C=O on the surface. The influence of nature of the precursor, pyrolysis conditions and presence of oxygen are studied in a fixed-bed reactor at 25 °C and atmospheric pressure for N₂/CO₂/O₂ feed stream. The presence of ultra micropores is found to be the most important parameter in absence of O₂ in feed stream while the selective adsorption of CO₂ over O₂ and N₂ takes place because of the surface chemistry of the activated carbon. Although there is no trend in the C K-edge spectra of fast and slow pyrolysis products, the selectivity of adsorbents for CO₂ over O₂ can be explained by the presence of C-O and C=O functional groups on the surface. SD-SP AC results in a longer t_b of 7.5 min, and higher adsorption capacity of 78.1 mg/g, but less selectivity, 2.8, in the presence of O₂. For the SD-SP AC, the CO₂ uptake is improved by 20% in absence on N₂. Besides, all adsorbents are regenerated to more than 94% of their initial adsorption capacity in ten cycles.

Chapter 5 Enhanced CO₂ Adsorption Using MgO-Impregnated Activated Carbon: Impact of Preparation Techniques

A similar version of this chapter has been published in the Journal of Industrial & Engineering Chemistry Research.

- *Shahkarami, S.; Dalai, A. K.; Soltan, J. Enhanced CO₂ Adsorption Using MgO-Impregnated Activated Carbon: Impact of Preparation Techniques. Ind. Eng. Chem. Res. 2016, vol. 55, pp. 5955-5964.*

In addition, some parts of this chapter were presented at the following conferences and symposiums:

- Selective CO₂ Adsorption on Activated Carbons, 24th Canadian Symposium on Catalysis Ottawa, ON, Canada, May 8-11, 2016.
- Surface modification of activated carbon for CO₂ capture, 65th Canadian Chemical Engineering Conference, Calgary, Canada, October 2015

Contribution of the Ph.D. candidate

In consultation with supervisors, the experiments were designed and conducted by Sepideh Shahkarami. All the samples were prepared and impregnated by Sepideh Shahkarami. All characterizations were performed and the related data were analyzed by Sepideh Shahkarami. The data analyses and interpretations were conducted by Sepideh Shahkarami. All of the written text was prepared by Sepideh Shahkarami and all the experiments were discussed with Drs. A.K. Dalai and J. Soltan.

Contribution of this chapter to the overall study

In the Chapters 3 and 4, it was shown that the CO₂ adsorption capacity and selectivity of the activated carbon can be optimized by a number of parameters including activating agent,

carbonization conditions and the nature of precursors. However, CO₂ adsorption capacity of activated carbon is limited by adsorption conditions. CO₂ adsorption capacity decreases with increasing temperature and decreasing the CO₂ content in gas mixture. The main objective of the research presented in this chapter is to present the effects of metal impregnation of the activated carbon on CO₂ adsorption performance of this adsorbent for CO₂ separation at low and moderate temperature conditions.

Abstract

The development of a facile and sustainable approach to produce magnesium oxide (MgO) activated carbons impregnated through a single-step activation of biochar is reported. In a single-step activation process, biochar is impregnated with 3 and 10 wt. % of magnesium salt solutions followed by steam activation. In a two-step method, activated carbon, the product of steam activation of biochar, is impregnated with magnesium salt using the incipient wetness and excess solution impregnation process and calcined. The impacts of activation method, impregnation method, and metal content are evaluated, and the product qualities are compared in terms of porosity and surface chemistry. The sorbents are then used for CO₂ capture in low partial pressure of CO₂ at 25 and 100 °C from a feed containing 15% CO₂ in N₂ in a fixed-bed reactor. The incipient wetness of activated carbons results in the highest CO₂ uptake (49 mg/g) at 25 °C, while single-step impregnation of biochar with rinsing step yields the largest surface area (760 m²/g) and the second highest CO₂ uptake (47 mg/g). The increase in Mg content from 3 to 10 wt % results in the smaller surface area and higher CO₂ uptake suggesting that the metal content has a greater impact than porosity and surface area. Rinsing the Mg impregnated activated carbon with water results in the larger surface area and higher CO₂ uptake in all samples. Moreover, the CO₂ adsorption runs at 100 °C shows a 65% increase using MgO impregnated activated carbon as compared to steam activated carbon indicating that MgO impregnation of activated carbon can overcome the limitation of using nontreated activated carbon at moderate operating temperature of 100 °C and low partial pressure of CO₂ of 15 mol %.

5.1 Introduction

Although the CO₂ adsorption capacity of activated carbon decreases with temperature and at low partial pressure of CO₂, the surface properties and adsorption behavior of activated carbons can be enhanced by amine treatment or metal impregnation of activated carbon. Increase in CO₂ adsorption capacity and high selectivity have been reported by modifications of the surface chemistry of the porous materials by incorporating basic sites of metal oxides that can interact with acidic CO₂. Impregnation of activated carbon with basic metal oxides can improve the surface chemistry and adsorption capacity of activated carbons for post-combustion carbon capture^{13,14,141,142}. MgO is available in natural minerals and can be produced in large quantities at low cost¹⁵. Chemisorption of CO₂ at temperatures below 200°C on MgO is highly selective and needs a lower regeneration energy as compared to other metal oxides^{15,16,143}. The interaction between the adsorbed CO₂ and the basic sites is weaker than that in the case of other alkali metal oxide which explains the lower working temperature of this adsorbent for CO₂ separation^{15,144}. The CO₂ adsorption sites on MgO are associated with low coordinated O²⁻ ions^{15,145} and the basicity of the O²⁻ mainly depends on its coordination. CO₂ interacts with basic O²⁻ to form a monolayer of CO₃²⁻¹⁴⁵. The small surface area MgO particles results in the formation of a termination layer of carbonate on the surface which limits the further reaction of the magnesium oxide with CO₂¹⁴⁶. Because the CO₂ uptake of MgO is rather small and to enhance the adsorption performance of MgO, mesoporous MgO is proposed for CO₂ adsorption applications^{15,144,146}. The facile mass transport in mesoporous MgO with large surface area (~120–136 m² g⁻¹) results in an enhanced CO₂ uptake as compared to the MgO nanoparticles which is mostly attributed to its large surface area¹⁴⁶. Bhagiyalakshmi et al.¹⁴⁴ reported 8 wt. % CO₂ uptakes on mesoporous MgO (250 m² g⁻¹) as compared to 1-2wt. % CO₂ uptake on nonporous MgO at 25°C. Compared to mesoporous MgO, the mesoporous carbon stabilized MgO nanoparticles produced from the fast pyrolysis of MgCl₂ loaded biomass exhibit a much higher adsorption capacity (240 mg/g at 80 °C), selectivity (112 and 11 over N₂ and O₂, respectively) and stability for CO₂ separation¹⁴³. In the pyrolysis process, MgO acts as an in situ template to form the porous structure¹⁴³ and increase in surface area from 14 to 306 m² g⁻¹ was reported. With regard to the impact of porosity and coordination of O²⁻ in mass transport and basic properties of MgO based materials, a practical method to produce MgO impregnated

activated carbon with mesoporous structure and high surface area can be an alternative for CO₂ separation at moderate temperature.

Metal impregnation of activated carbon is usually performed using either incipient wetness or excess solution impregnation followed by a calcination^{142,147}. Merging the activation and calcination processes into one step can be an efficient and practical alternative to produce metal impregnated activated carbon¹⁴². In this method, biochar is impregnated using excess salt solution and then activated with steam at the desired conditions. In addition, metal content and rinsing of the samples can impact the adsorption behavior and CO₂ uptake of the impregnated activated carbons¹⁴.

In this work, in a single-step process, biochar was impregnated with MgO followed by steam activation. In a two-step process, biochar was activated by steam followed by MgO impregnation and calcined. The impacts of preparation methods, metal content and rinsing step on physical and chemical properties and CO₂ uptake of the activated carbons in a binary mixture of CO₂/N₂ is evaluated.

5.2 Materials and methods

Biochar, the feedstock, was produced by the fast pyrolysis of whitewood(same as the bichoar used in Chapter 3) and provided by Dynamotive Energy Systems Corporation (BC, Canada). The particle size range of 178–710 µm was collected for activation processes. Activated carbon used in this study was produced through steam activation of whitewood biochar as described in section 3.2.2 and Appendix A. For activation of biochar, appropriate amount of biochar was loaded in a fixed bed reactor and heated to 700 °C with the heating rate of 3°C/min under nitrogen at the flow rate of 140 standard mL/min (STP). Then, steam was injected into the reactor with the steam-to-carbon mass ratio of 1.06 for 1.4 h. The reactor was then cooled down to room temperature under nitrogen flow¹. MgO impregnated activated carbons are produced through single-step process of steam activation of MgO impregnated biochar and two-step process of production of steam activated carbon from biochar followed by MgO impregnation of steam activated carbon and calcination. In all cases, the ratio of Mg weight to the

impregnated activated carbon is calculated and considered as metal loading. Magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was obtained from Aldrich (Milwaukee, USA).

5.2.1 Excess solution impregnation of biochar

Prior to the impregnation, biochar was dried at 100 °C overnight. Then, the biochar was treated with magnesium nitrate of an appropriate concentration in 100 ml water for 15 h. After that, the sample was dried at 100°C for 15 h in an oven. The procedure was followed by the steam activation process. In order to evaluate the impact of rinsing step on the CO_2 adsorption of impregnated activated carbons, the samples were prepared with and without rinsing after steam activation. The impregnated activated carbons were rinsed with distilled water and then the samples were dried at 100°C for 15 h in an oven. The produced samples are denoted as 3Mgo-B: 3 wt. % MgO loaded biochar, 3MgO-B-R: 3 wt. % MgO loaded biochar-rinsed, 10MgO-B:10 wt. % MgO loaded biochar and 10MgO-B-R:10 wt. % MgO loaded biochar- rinsed. The details of impregnation conditions, activation yield and weight loss after rinsing are described in Table E1 of Appendix E.

5.2.2 Excess solution impregnation of activated carbon

Activated carbons, prepared through the steam activation of biochar, were impregnated in 100 ml water with metal nitrate of an appropriate concentration (3 and 10 wt. %) for 15 h. The mixtures of activated carbon and solutions of metal nitrate were then dried in the oven for 15 h. The procedure was followed by calcination at 325 °C for 4 h. The impregnated activated carbons were then rinsed and dried at 100 °C for 15 h in an oven. The produced samples were denoted as 3Mgo-AC: 3 wt. % MgO loaded activated carbon, 3MgO-AC-R: 3 wt. % MgO loaded activated carbon-rinsed, 10MgO-AC:10 wt. % MgO loaded activated carbon and 10MgO-AC-R:10 wt. % MgO loaded activated carbon-rinsed. The details of the impregnation conditions, activation yield and weight loss after rinsing and calcination conditions are described in Table E2 of Appendix E.

5.2.3 Incipient wetness impregnation of activated Carbon

Prior to the impregnation, the total pore volume of the sample was estimated by BET measurements. Metal nitrate with an appropriate concentration was dissolved in the water, and the solution was added to the activated carbon drop by drop. The mixture is kept at room temperature for 15 h. Then the sample was dried at 100 °C for 15 h in an oven. The procedure was followed by calcination at 325 °C for 4h. The produced samples are denoted as 3MgO-AC-DRY: 3 wt % MgO incipient impregnated activated carbon and 10MgO-AC-DRY: 10 wt. % MgO incipient impregnated activated carbon

5.2.4 Characterization

The BET surface area, total pore volume and pore size distribution of the activated carbons were determined as described in section 3.2.4. The thermal stability of the activated carbons was determined by Thermogravimetric Analyzer (Q500, TA Instruments, USA) in the temperature range of 30-700 °C at a heating rate of 5°C/min under nitrogen flow. Powder X-ray diffraction (XRD) data were collected with a D8 Advance (Bruker, USA) with a rotating copper anode (Cu K- α) and an INEL CPS-120 detector, operating in the 2 θ range of 10- 90° with a scan rate of 2°. The temperature-programmed desorption (TPD) of carbon dioxide was carried out using an Autosorb IQ (Quantachrome, USA). The sample was placed in the reactor and heated in helium flow of 50 ml/min at 150°C for 30 min to remove the physically adsorbed CO₂. The sample was then cooled down to 50 °C, and the TPD profile was recorded by increasing the temperature from 50 to 700 °C at a heating rate of 10°C /min under 50 mL/min of He.

5.2.5 CO₂ adsorption measurements

The CO₂ adsorption properties of the prepared samples were evaluated by passing the CO₂/N₂ gas mixture through the one-inch fixed-bed Inconel tubular reactor using a dual channel Micro-Gas Chromatograph (490 micro-GC, Agilent Technologies Inc., USA) equipped with a micro-thermal conductivity detector (μ TCD) as described in **section 4.2.6** . Adsorption capacity and selectivity were calculated as described in section 2.3.1. The reactor was loaded with 5 g of activated carbon and pre-heated at 160 °C for 2 h under N₂ flow of 50ml/min before the adsorption experiments. After cooling down to desired temperature, the CO₂/N₂ feed stream

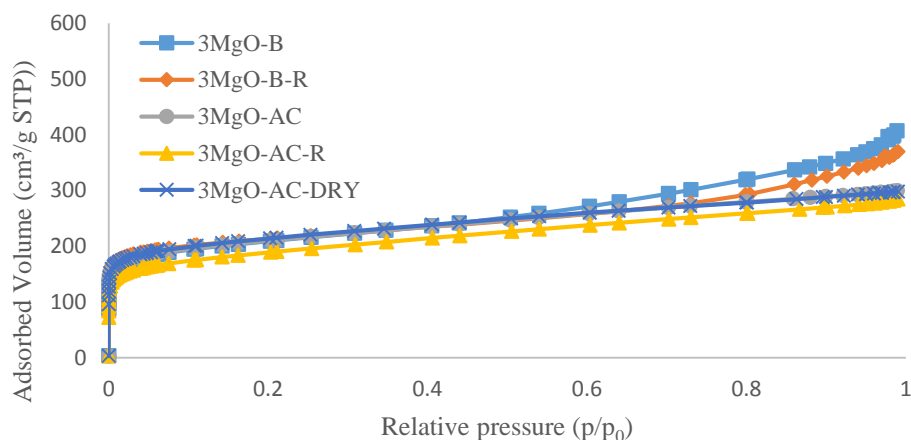
(15/85 mol. %) was passed through the reactor at 50 SmL/min. The adsorption process was continued, and the inlet flow rates, outlet flow rates, and CO₂/N₂ mole fractions were recorded until saturation. All the experiments were repeated twice, and average results are reported.

5.3 Results and discussion

5.3.1 Material characterization

In our preliminary experiments, activated carbon impregnated with 3, 10, 20 and 30 wt. % magnesium are prepared by incipient wetness impregnation method and their physical properties and their performances are evaluated at 25 and 100 °C. The surface area and pore volume of prepared adsorbent showed a significant decrease at ≥ 20 wt. % content and more. The CO₂ uptake in all cases increased with increase in metal loading but the increase in breakthrough time and CO₂ uptake were not remarkable at ≥ 20 wt. % content. Therefore, we limited the magnesium concentration to 3 and 10 wt. % in this work.

Figure 5-1 and Table 5-1 show the nitrogen adsorption-desorption isotherms at 77K and textural properties of all samples, respectively. The nitrogen sorption isotherms of all samples show the type IV patterns of mesoporous materials with hysteresis loops of Type H4, indicating the presences of slit-shaped pores mainly in micropore size distribution range³⁶.



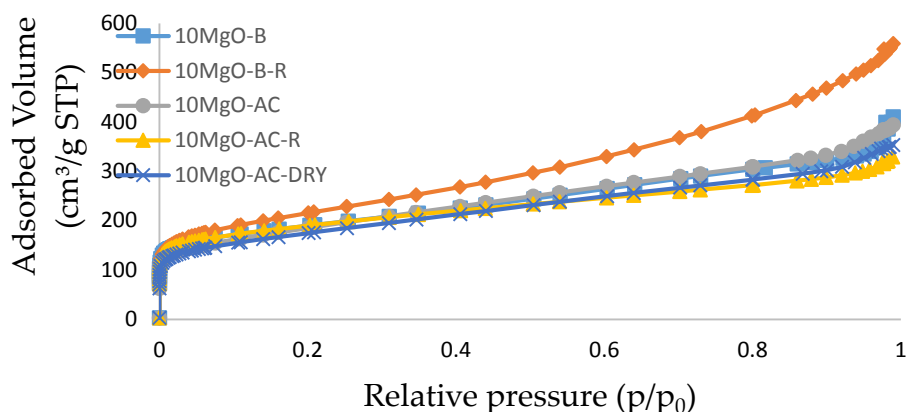


Figure 5-1: N₂ adsorption-desorption isotherms at 77 K

Although, the nitrogen sorption isotherm do not show the considerable difference, and pore volumes remain in the same range, with the exception of 10MgO-B-R, the pore size distributions of samples show some variation (Figures 5-2 and 5-3).

Table 5-1: Physical characteristics of adsorbents

	3MgO-B	3MgO-B-R	3MgO-AC	3MgO-AC-R	3MgO-AC-Dry
BET surface area (m ² /g)	741	760	667	743	760
Total pore volume (cm ³ /g)	0.421	0.560	0.348	0.403	0.399
Ultra-micro-pore volume, cm ³ /g	0.162	0.175	0.128	0.188	0.089
Micro-pore volume, cm ³ /g	0.221	0.222	0.191	0.197	0.232
Meso-pore volume cm ³ /g	0.197	0.321	0.157	0.201	0.165
Macro-pore volume cm ³ /g	0.002	0.017	0.000	0.005	0.003
	10MgO-B	10MgO-B-R	10MgO-AC	10MgO-AC-R	10MgO-AC-Dry
BET surface area (m ² /g)	676	760	651	671	615
Total pore volume (cm ³ /g)	0.547	0.801	0.337	0.449	0.496
Ultra-micro-pore volume, cm ³ /g	0.143	0.123	0.122	0.106	0.123
Micro-pore volume, cm ³ /g	0.170	0.164	0.173	0.139	0.147

Meso-pore volume cm ³ /g	0.293	0.589	0.161	0.309	0.331
Macro-pore volume cm ³ /g	0.083	0.049	0.002	0.001	0.017

As shown in Table 5-1, 3MgO-B-R and 10MgO-B-R have the largest surface area and pore volume. The increase of pore volume of MgO-B-R compared to steam activated carbon (0.556 cm³/g) implies that impregnation of biochar may have catalyzed some steam activation process. This increase in of the pore volume is also confirmed by the DFT pore size distribution curves shown in Figures 5-2 and 5-3. These results indicate that, regardless of metal content, the excess solution impregnation of biochar leads to larger surface area and pore volume. This means that the main impact of the preparation is to alter the pore size distribution without a significant change in surface area. The rinsing step also increases the pore volume and surface area. The lower surface area and pore volume of unrinsed sample can be attributed to the deposition of magnesium oxides on the walls and/or blocking the smaller pores of the activated carbons¹⁴⁸. Despite the different impacts of the preparation method, 10 wt. % metal content results in larger mesopore volume and total pore volume of the samples while micropore pore volume decreases. The standard deviation of measured surface area in all not-rinsed samples is less than ± 4 and in 3 and 10 wt. % MgO impregnated samples with rinsing step were ± 13 and ± 17 , respectively.

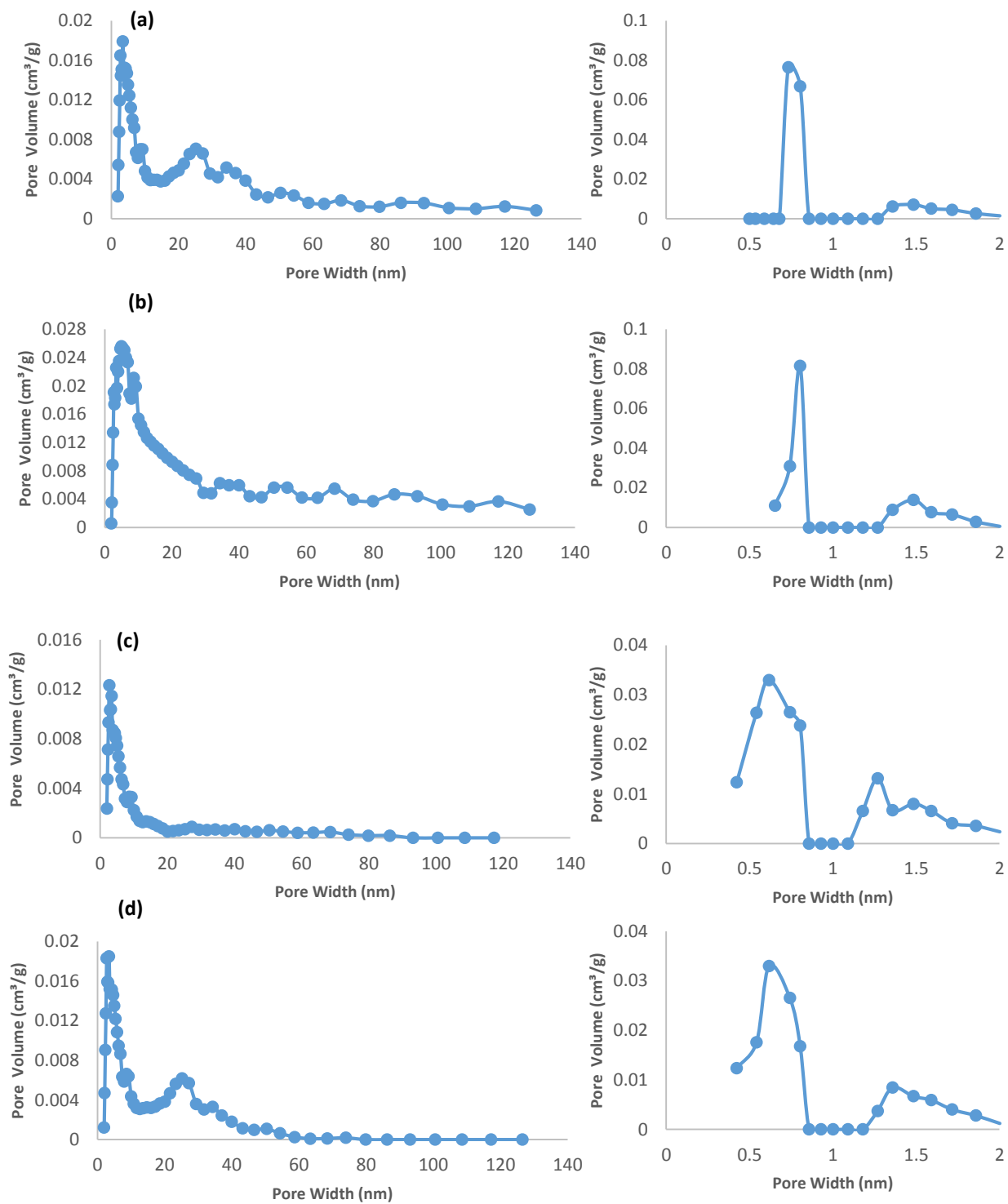
The TG/DTG profiles of thermal decomposition of the precursors are provided in Figure 5-4. A peak at 180 °C followed by a broad shoulder at 210 °C is associated with the loss of physically absorbed water on the activated carbon surface. A sharp peak at 325°C and a distinct mass loss of the sample indicate the thermal decomposition of precursors and formation of MgO on activated carbon surface¹⁴⁹.

The XRD patterns of the 10 wt. % impregnated samples are shown in Figure 5-5. The XRD patterns of samples show five diffraction peak at 2θ of 37.1, 43.1, 62.5, 74.7 and 78.6 which indicate (111), (200), (220), (311), and (222) lattice plans of MgO, respectively¹⁴³. As it can be observed in Figure 5-5, the preparation method impacts intensities of the reflections and FWHM (full width at half maximum) values in the XRD pattern. The wide FWHM of MgO-AC and MgO-AC-DRY indicate that the average crystallite size of MgO on these samples is smaller than MgO-B. The increase in intensity and narrow FWHM values of the diffraction peak in MgO-B implies that MgO crystallite size on carbon samples increases in single-step

impregnation of activated carbon. The average MgO crystallite size is calculated using the Scherrer equation(Eq. 5-1)¹⁵⁰.

$$t = \frac{K * \lambda}{B * \cos \theta_B} \quad (5-1)$$

where t is the average crystal size, K is the constant (dependent on crystallite shape), λ is the X-ray wavelength, β is the FWHM of the reflection peak, and θ_B is the Bragg angle. The average MgO crystallite size of 10MgO-B, 10MgO-AC and 10MgO-AC-DRY are 16.7, 1.8 and 2.6 nm.



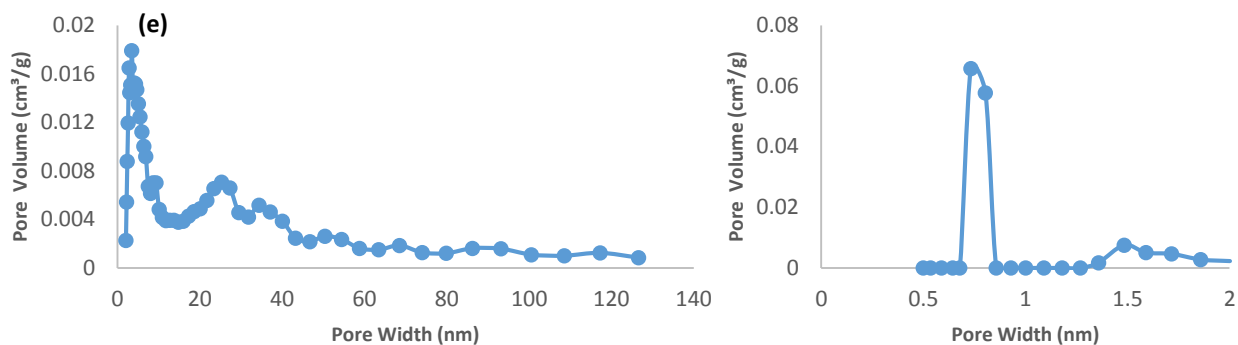
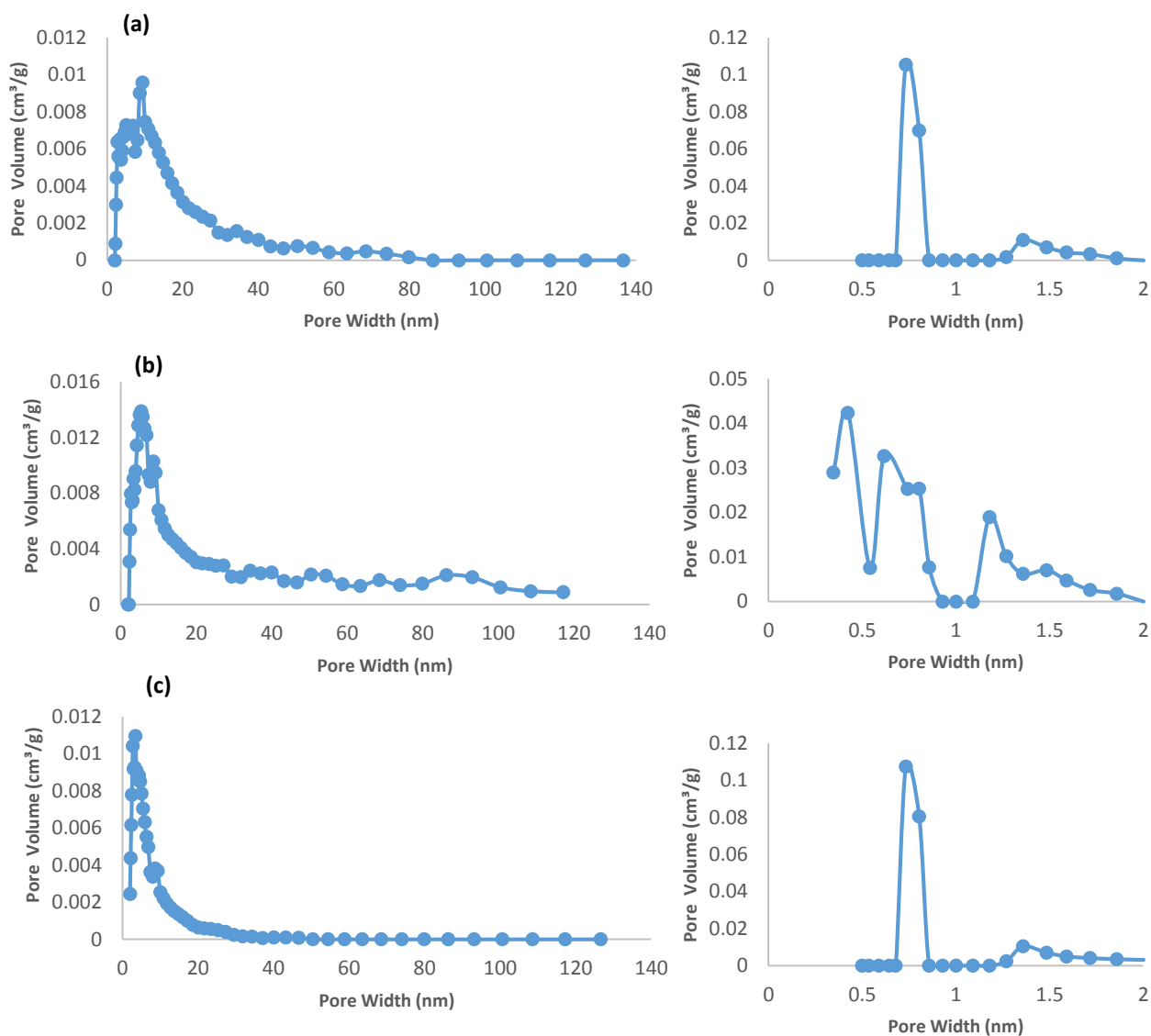


Figure 5-2: Pore size distributions of (a) 10MgO-B, (b) 10MgO-B-R, (c) 10MgO-AC, (d) 10MgO-AC-R and (e) 10MgO-AC-DRY determined from the N₂ and CO₂ adsorption isotherms at 77 K and 273 K using a NLDFT analysis



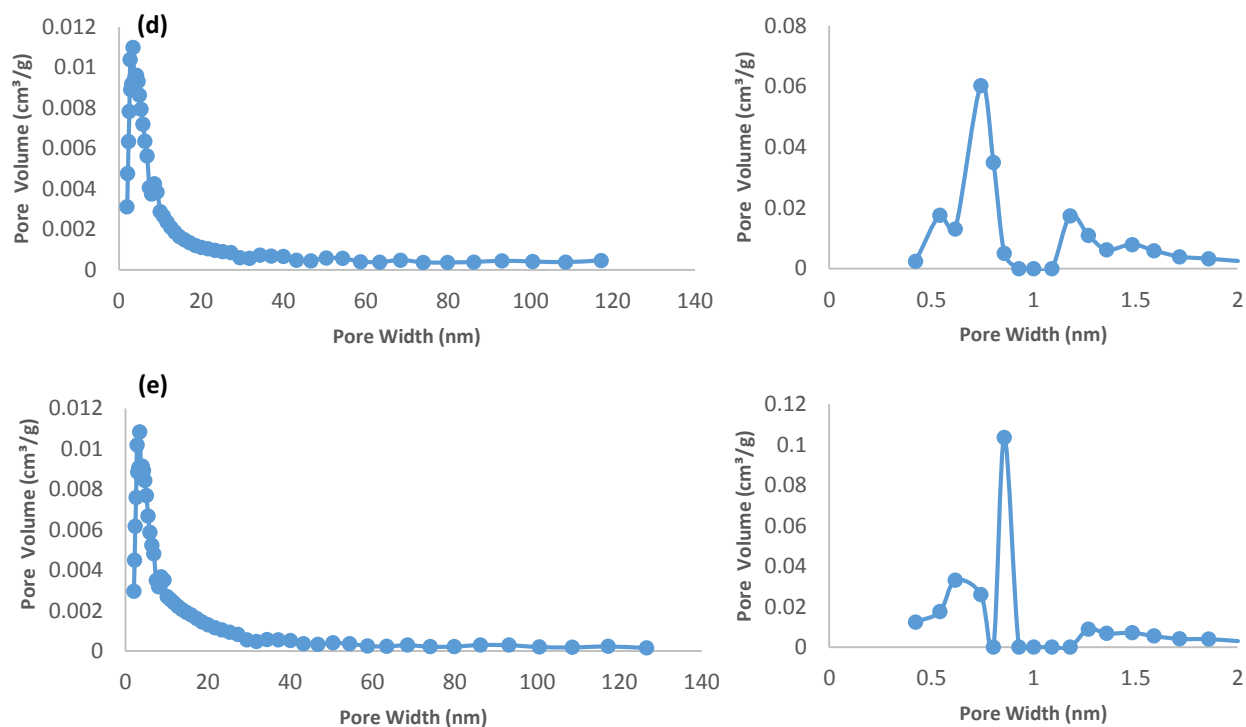


Figure 5-3: Pore size distributions of (a) 3MgO-B, (b) 3MgO-B-R, (c) 3MgO-AC, (d) 3MgO-AC-R and (e) 3MgO-AC-DRY determined from the N_2 and CO_2 adsorption isotherms at 77 K and 273 K using a NLDFIT analysis

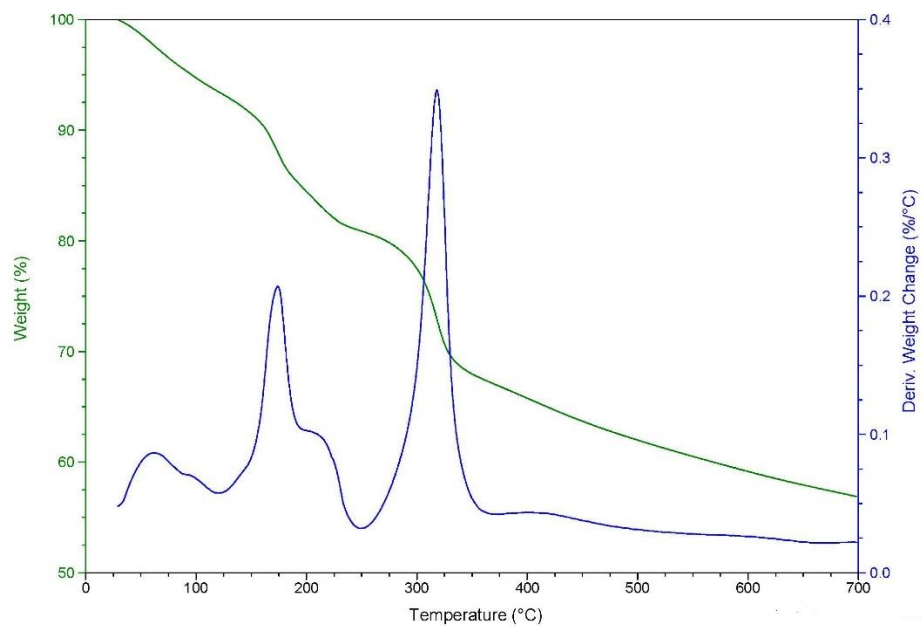


Figure 5-4: TG-DTG profiles of 10MgO-AC heated from 30 to 700°C in N_2 flow

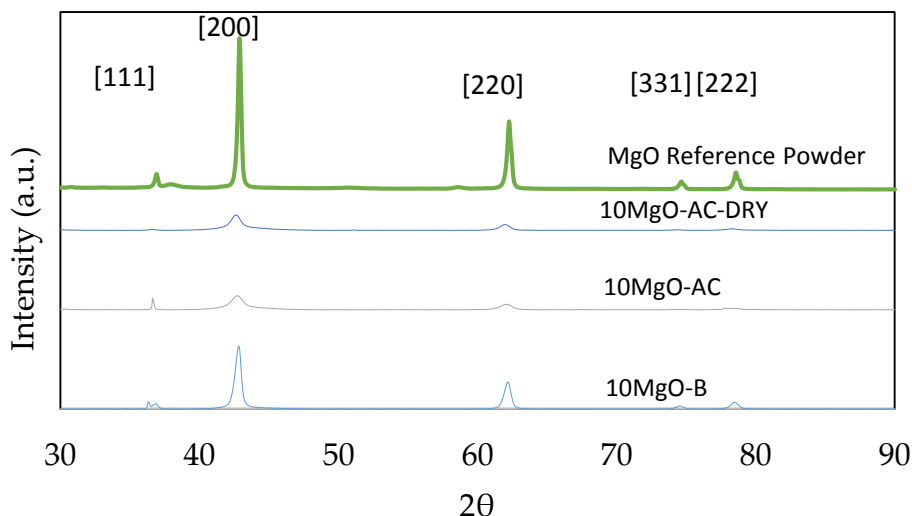


Figure 5-5: Powder X-ray diffraction (XRD) patterns of 10 wt. % MgO loaded activated carbon samples

Figure 5-6 demonstrates the TPD curve for CO₂ adsorbed 10MgO-AC-DRY. The sample is heated at 150°C prior to the measurement, so the initial weight loss due to the physisorbed CO₂ cannot be seen in the curve. The broad weight loss from 520 to 600°C is due to the chemisorbed CO₂ indicating that the complete regeneration occurs only by heating at 600°C.

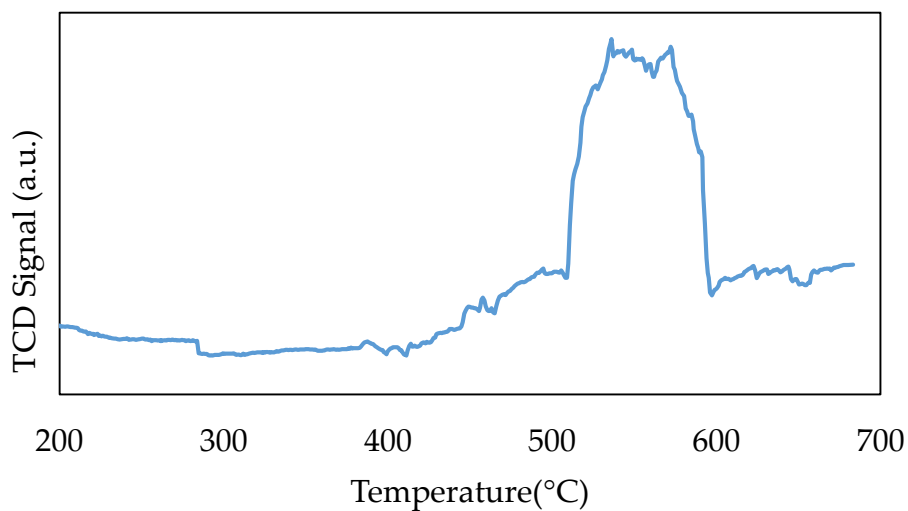


Figure 5-6: TPD Profile of 10 wt. % MgO loaded activated carbon (10MgO-AC)

5.3.2 CO₂ adsorption on impregnated activated carbon

The adsorption curves of 3 and 10 wt. % loaded activated carbons and CO₂ adsorption capacity and breakthrough time in CO₂/N₂ feed steam at 25 °C are shown in Figure 5-7 and Table 5-2, respectively. With the exception of 10MgO-B, increase in metal oxide content enhanced the breakthrough time and CO₂ adsorption capacity, regardless of preparation method, and this is believed to be because of an increase in chemisorption of CO₂ on activated carbon. Rinsing step increases surface area, pore volume and CO₂ uptake of samples in both biochar and activated carbon samples. Impregnation of biochar with rinsing step results in the largest surface area and total pore volume and a significant increase in CO₂ uptake and breakthrough time.

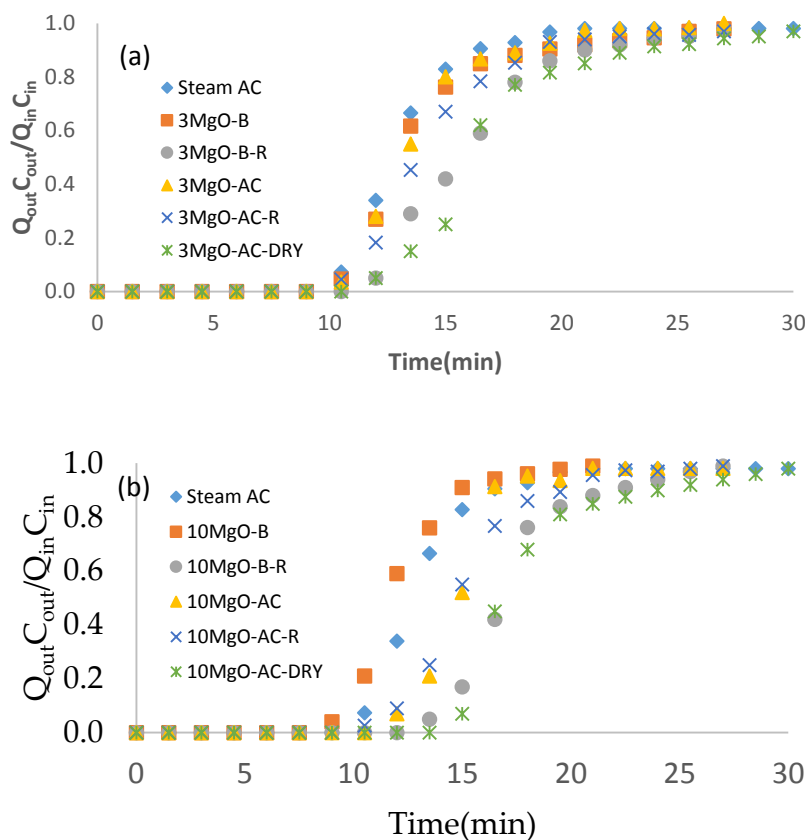


Figure 5-7: Breakthrough curves of 15% CO₂ in N₂ at 25°C on (a) 3 wt. % and (b) 10 wt. % MgO impregnated activated carbons

Although the similar increase is observed in impregnation of activated carbon (MgO-AC-R), the increase is more significant in 10 MgO-B-R. Regardless of their higher surface area, 3 wt. % loading of MgO on biochar and activated carbon does not have a considerable impact on the breakthrough curve and adsorption capacity except for 3MgO-B-R and 3MgO-AC-DRY indicating that metal content is more influential than surface area for CO₂ adsorption. The results also indicate that CO₂ uptake of 10MgO-AC-DRY increased by 40% as compared to that for untreated activated carbon. MgO-B-R activated carbon with well-dispersed metal particles and higher surface area than untreated activated carbon, exhibits a notable increase in both breakthrough time and CO₂ uptake. These results suggest that combination of impregnation and activation step into a single-step process can be an alternative technique to produce metal impregnated activated carbon for CO₂ adsorption.

Our initial evaluation suggests that impregnation of biochar through single-step process is an effective technique for production of CO₂ sorbents; hence, 10MgO-B-R was chosen for further investigation. As it is shown in Figure 5-8, CO₂ physisorption on activated carbon decreases with temperature due to exothermic nature of this process. The adsorption of CO₂ at 100 °C in the CO₂/N₂ feed stream is conducted in the same experimental set-up. CO₂ adsorption breakthrough curves of untreated activated carbon and 10MgO-B-R at 25 and 100 °C are shown in Figure 5-8. The CO₂ uptake at 100 °C exhibits a significant increase from 15.7 to 25.8 mg/g after treatment indicating that metal impregnation has a potential for moderate temperature post-combustion carbon capture at the lower content of CO₂.

For a practical application of an adsorbent, stability and regenerability are also important. Figure 5-9 shows the regenerability of 10MgO-B-R in five cycles. The adsorption index (%) is the ratio of CO₂ uptake of regenerated adsorbent to the virgin one¹¹⁸. In the multicycle study, the adsorbent is fully regenerated at 600°C keeping more than 93% of the initial adsorption capacity.

Table 5-2: CO₂ adsorption capacities and breakthrough time at 25° C

	AC	3MgO-B	3MgO-B-R	3MgO-AC	3MgO-AC-R	3MgO-AC-DRY
CO ₂ adsorption						
capacity (mg _{adsorbed} /g adsorbent)	35	38	44	38	40	46
Breakthrough time (s)	602	637	720	635	641	720
Standard deviation	±0.3	±0.4	±0.5	±0.9	±0.8	±0.8

	AC	10MgO-B	10MgO-B-R	10MgO-AC	10MgO-AC-R	10MgO-AC-DRY
CO ₂ Adsorption						
capacity (mg _{adsorbed} /g adsorbent)	35	34	47	40	42	49
Breakthrough time (s)	602	563	811	694	664	874
Standard deviation	±0.3	±0.8	±0.6	±0.8	±1.0	±0.5

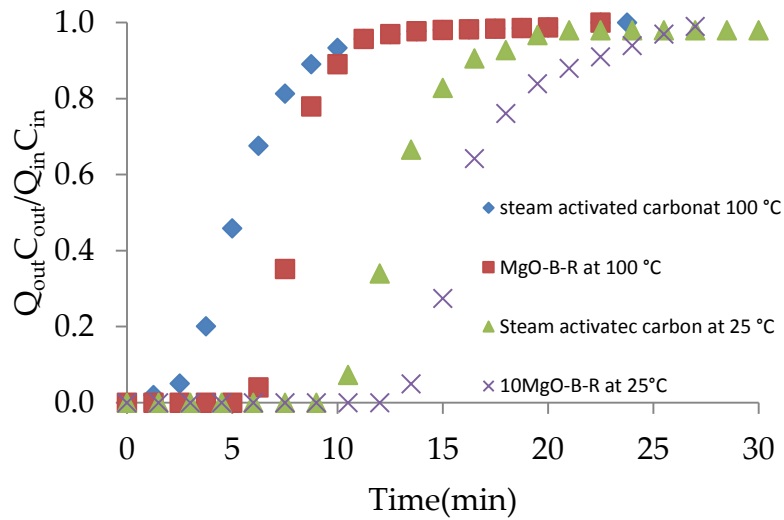


Figure 5-8: CO₂ adsorption on non-treated activated carbon and 10MgO-B-R at 25 and 100 °C

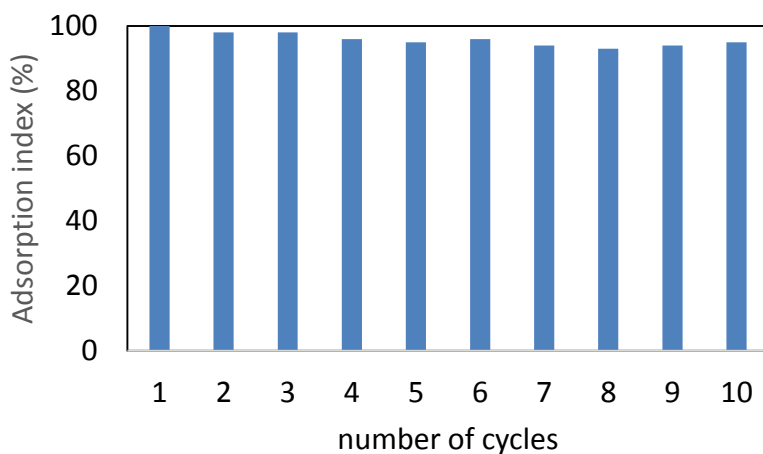


Figure 5-9: Cyclic CO₂ adsorption of 15% CO₂ in N₂ at 25°C on 10MgO-B-R

5.4 Conclusions

MgO impregnated activated carbons are produced using different preparation techniques and compared to not-treated activated carbon in terms of pore size distribution, surface area, CO₂ uptake and breakthrough time at 25 and 100°C and for adsorption under a binary mixture of CO₂/N₂. Preparation method has the greatest impact on the surface area, porosity and dispersion of metal in activated carbons. Surface area and pore size distribution are impacted by both metal content and preparation method. Largest surface area of 760 m²/g is developed using the excess solution impregnation of biochar with rinsing step. 10 wt. % MgO loaded activated carbon produced through incipient wetness with a surface area of 615 m²/g has the highest CO₂ adsorption capacity (49 mg/g) suggesting that preparation method and metal content are more important than surface area and porosity of the samples. Rinsing step before calcination can positively impact the impregnation of MgO on activated carbon for CO₂ adsorption.

Chapter 6 Equilibrium and Modeling of Isothermal Fixed-Bed CO₂ Adsorption

A similar version of this chapter has been submitted to the International Journal of Greenhouse Gases Control:

- *Shahkarami, S.; Ghasemi, M.; Dalai, A. K.; Soltan, J.; CO₂ Adsorption on Activated Carbon: Equilibrium, and Kinetics of Fixed-Bed Isothermal Adsorption, international journal of greenhouse gas control, under communication.*

In addition, some parts of this chapter were presented at the following conference:

- Enhanced CO₂ Adsorption on Activated Carbon, 66th Canadian Chemical Engineering Conference, Quebec City, QC, October 16-19, 2016.

Contribution of the Ph.D. candidate

In consultation with supervisors, all the activated carbon samples were prepared by Sepideh Shahkarami. All the experiments were planned and conducted by Sepideh Shahkarami. The samples characterizations were performed and the related data were analyzed by Sepideh Shahkarami. Mass transfer model and all the related equations and calculation were selected by Sepideh Shahkarami. The adsorption isotherms were derived and fitted by Sepideh Shahkarami with assistance of Amir Abolhassani. The data analyses and interpretations were conducted by Sepideh Shahkarami. The program code in Python was written by Dr. Mehdi Ghasemi. All of the written text was prepared by Sepideh Shahkarami and all the experiments were discussed with Drs. A.K. Dalai and J. Soltan.

Contribution of this chapter to the overall study

This chapter contains the development of an isothermal mass transfer model for CO₂ adsorption in a binary mixture under post-combustion capture conditions. Additionally, the experimental results were compared to model prediction to validate the model.

Abstract

The equilibria and kinetics of CO₂ adsorption on microporous activated carbon have been studied using a fixed-bed adsorption set-up. Adsorption equilibria of pure component were measured at 0, 25, 50 and 75 °C on activated carbon bed and the data were fitted with the Langmuir model. The breakthrough curves were obtained using CO₂ balanced in N₂ at feed concentrations of 5%, 15% and 25 mol.%; temperatures of 25, 45, 65 and 85 °C and feed flowrates of 30, 50 and 70 ml/min. Results indicated that temperature has the greatest impact on breakthrough time and adsorption capacity. Decrease in feed flowrate increases adsorption capacity and breakthrough time while the adsorption capacity was independent of the initial CO₂ content.

A mathematical model based on the bilinear driving force (bi-LDF) model was developed to calculate the overall mass transfer coefficient. The model describes mass transfer due to bulk, Knudsen and intracrystalline diffusion. The total porosity of the bed was calculated by taking the particle porosity and bed porosity into account. The reproducibility of adsorption breakthrough curves of the model was validated with experimental data. In all cases, the predicted breakthrough curves were in agreement with the experimental data. It was shown that for CO₂ adsorption on microporous activated carbon, the controlling mass transfer step is micropore mass transfer resistance.

6.1 Introduction

To design a CO₂ adsorption process, development of a mass transfer model to describe the transport of CO₂ from a gas mixture to the adsorption sites of the activated carbon and adsorption model of the bed is essential. Using independently acquired equilibrium data, the model can be used to predict the breakthrough curves and adsorption behavior of the bed without extensive experimental data. In most of numerical studies on CO₂ adsorption, linear driving force (LDF) model is to approximate the adsorption rate^{151–154}. The bilinear driving force (bi-LDF) model, proposed by Azevedo and Rodrigues,¹⁵⁵ provides a close approximation of the mass balances in macro-pores and in micro-pores. In this model, both macro-pores and the micro-pores diffusion are represented by LDF model.

The objective of this work is to accurately measure the kinetic data and diffusion parameters, and to develop an isothermal mass transfer model for CO₂ adsorption on a fixed-bed of microporous KOH activated carbon bed in a binary mixture of CO₂/N₂ feed stream. The flow pattern is described as an axially dispersed plug flow model and the adsorption rate is represented by a Bi-LDF model that treats the macro pore and micropore resistances independently⁹⁶. The bed porosity, particle size, density, mass transfer coefficients, Langmuir constants are calculated independently.

6.2 Material and methods

6.2.1 Activated carbon

The KOH activated carbon was prepared from biochar (by-product of fast pyrolysis of whitewood). “The as-received biochar was sieved, and particle size range of 150-355 μm was collected for activation process. Biochar was impregnated with KOH in 100 ml of water with biochar to KOH mass ratio of 0.81 on a dry basis. After 15 h mixing at the room temperature, the mixture was dried in an oven at 110 °C for 15 h. The dried sample was then loaded in the tubular reactor under a nitrogen flow of 240 SmL/min and heated to 300 °C and held for 1 h at 300 °C¹⁰⁸. The temperature of the reactor was then increased to 775 °C with a heating rate of 3 °C/min and held at this temperature for 2 h before cooling down to room temperature. The sample was then washed with hot water, followed by 0.1M HCl, and finally distilled water to remove the soluble salts and the potassium compounds”^{1,109,110}. The sample was then dried in an oven overnight at 110 °C. Finally, the prepared activated carbon was sieved, and particle size range of 150-355 μm was collected for activation processes¹. The N₂ and CO₂ adsorption isotherms were measured at 77 and 273 K, respectively, using ASAP 2020 (Micromeritics Instruments Inc.) and the micropore size distribution and particle pore volume($V_{p,b}$) was determined using the non-local Density Function Theory (NLDFT)⁴². The specific surface area was determined using BET (Brunauer, Emmett, and Teller) method. Skeletaldensity (ρ_s) was measured using helium pycnometer (Quantachrome instrument, USA). Other physical properties of produced activated carbon are described in Chapter 2 (Eq. **2-36** and **2-37**).

6.2.2 Adsorption isotherm

The equilibrium data of CO₂ and N₂ adsorption on the collected activated carbon samples were measured in the adsorption experimental set-up with a packed column at 0, 25 and 50 and 75 °C. The adsorption capacity of CO₂ in a fixed-bed reactor was calculated using CO₂ diluted with argon. Before the adsorption measurements, the bed was pre-heated at 150 °C for 15 h. The total flow rate was maintained constant at 50 ml/min and the bed temperature was controlled using a K-type thermocouple and temperature controller (2416, Eurotherm, USA). The details of the adsorption set-up and the related calculation are reported before^{1,53}. Physical properties of the fixed-bed are given in Table 6-1. The calculated experimental data are then fitted to Langmuir isotherm (Eq. 6-1).

$$q_{ci}^* = \frac{q_{si} b_i p_i}{1 + b_i p_i} \quad (6-1)$$

where q_{si} is the saturation capacities (temperature-independent), b_i is the isotherm parameter for gas i , and p_i is the partial pressure of component i . In this equation, the isotherm parameter is calculated using Arrhenius-type temperature dependence (Eq. 6-2):

$$b_i(T) = b_i(T_0) \exp\left(\frac{-\Delta H_{adsi}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (6-2)$$

The isotherm parameters are calculated from the independent fits of the single component data to the Langmuir isotherm.

6.3 Mathematical model and solution method

The adsorption models are used to study the gas transfer from gas mixture to a solid sorbent and predict the change in concentration profiles along the bed due to any changes in process conditions. A mass balance on an isothermal fixed-bed (Figure 6-1) was used to explain the mass-transfer process through a bed. The mechanism of CO₂ transfer for gas–solid adsorption includes diffusion through the film surrounding adsorbent particle and then diffusion into the macropores and micropores to the adsorption sites of adsorbent.

Table 6-1: Experimental parameters used in the simulation

Specific surface area	1461	m ² /g
Pore volume	5.8E-04	m ³
Bed length	0.030	m
Bed diameter	0.022	m
Total flowrate	50	ml/min
Skeletal density(ρ_s)	2111	kg/m ³
particle density(ρ_p)	952	kg/m ³
bulk density (ρ_b)	435	kg/m ³
bed porosity(ϵ_b)	0.543	
particle porosity(ϵ_p)	0.549	
total porosity(ϵ_t)	0.794	
Mean particle radius(R_p)	1.1E-04	m
mean pore radius(r_p)	6.54E-09	m

6.3.1 Model description

An isothermal bi-LDF was developed to study the CO₂ adsorption from a CO₂/N₂ gas mixture using a fixed-bed of KOH activated carbon. Bi-LDF model includes both macropore (molecular and Knudsen diffusions) and micropore resistances in a linear model. The following assumptions are considered in this model:

- The adsorption process is isothermal.
- An axially dispersed plug flow model describes the flow pattern in the fixed bed.
- The Bi- LDF model is used to calculate the adsorption rate.
- The radial gradient of pressure, velocity and concentration of the gases in the solid and the gas are negligible.
- The adsorption behaviors are described by the Langmuir isotherm model.

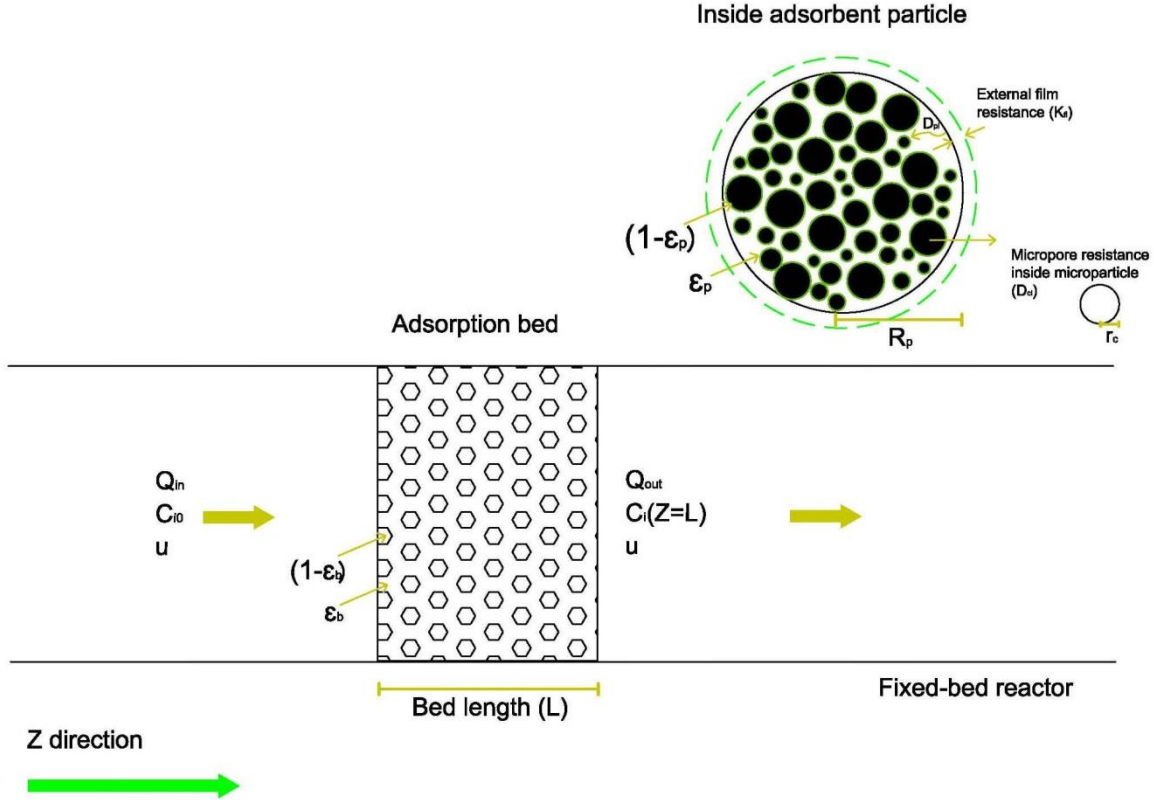


Figure 6-1: Schematic of mass transfer in a fixed bed reactor showing the mechanism of gas transfer to adsorption sites

The overall mass balance for the component i ($i = \text{CO}_2, \text{N}_2$) in the z direction (Figure 6-1) is given as Eq. 6-3¹⁵⁶:

$$\epsilon_t \frac{\partial c_i}{\partial t} + (1 - \epsilon_b) \rho_p \frac{\partial \bar{q}_{pi}}{\partial t} = -\epsilon_b u \frac{\partial c_i}{\partial z} + \epsilon_b \frac{\partial}{\partial z} \left(D_{ax} \frac{\partial c_i}{\partial z} \right) \quad (6-3)$$

In equation 6-3, the average adsorbed concentration of i (\bar{q}_{pi}) per unit of adsorbent particle mass is equal to concentration in gas phase of component i (c_{pi}) trapped in the macropores and average adsorbed concentration of component i (\bar{q}_{ci}) per unit of particle volume⁹⁶(Eq. 6-4):

$$\rho_p \bar{q}_{pi} = \epsilon_p c_{pi} + (1 - \epsilon_p) \rho_s \bar{q}_{ci} \quad (6-4)$$

Combining the macropore and micropore resistances into a bi-LDF model results in an overall adsorption using the bi-LDF rate equation (Eq. 6- 5) ¹⁰¹:

$$\rho_p \frac{\partial \bar{q}_{pi}}{\partial t} = k_{pi}(c_i - \bar{c}_{pi}) + \frac{15D_{ci}}{r_c^2}(1 - \varepsilon_p)\rho_s(q_{ci}^* - \bar{q}_{ci}) \quad (6-5)$$

Combining Equations 6-3 and 6-5 results in the mass balance of component i using bi-LDF model (Eq. 6-6):

$$\varepsilon_t \frac{\partial c_i}{\partial t} + (1 - \varepsilon_b) \left[k_{pi}(c_i - \bar{c}_{pi}) + \frac{15D_{ci}}{r_c^2}(1 - \varepsilon_p)\rho_s(q_{ci}^* - \bar{q}_{ci}) \right] = -\varepsilon_b u \frac{\partial c_i}{\partial z} + \varepsilon_b \frac{\partial}{\partial z} \left(D_{ax,i} \frac{\partial c_i}{\partial z} \right) \quad (6-6)$$

where k_{pi} is the effective LDF constant that represents the effects of external fluid film, molecular and Knudsen diffusion resistances in the macropores (Eq. 6-7 and 6-8):

$$k_{pi} = \frac{15\varepsilon_p D_{pi}}{R_p^2} \frac{Bi_i}{Bi_i + 1} \quad (6-7)$$

$$Bi_i = \frac{R_p k_{f,i}}{5\varepsilon_p D_{pi}} \quad (6-8)$$

“ Bi is the Biot number representing the ratio of internal macropore to the external film resistance; and D_{pi} is the effective macropore diffusivity corrected for the tortuosity of component i ”⁹⁶. D_{pi} is calculated as follows^{87,97}(Eq. 6- 9):

$$\frac{1}{D_{pi}} = \frac{1}{D_{K,i}} + \frac{1}{D_{m,i}} \quad (6-9)$$

In Equation 6-9, $D_{K,i}$ is the Knudsen diffusivity and $D_{m,i}$ is the macropore diffusivity. Knudsen and macropore diffusivity are calculated as described in Chapter 2 (Eq. 2-43 to 2-47)

The crystal diffusivity (D_{ci}) at any loading is a function of surface diffusion at zero loading multiplied by the thermodynamic correction factor of $\frac{\partial \ln p_i}{\partial \ln q_{ci}}$ ^{46,96} as follows (Eq. 6-10):

$$D_{ci} = D_{ci}^{\infty} \frac{d \ln(p_i)}{d \ln(q_{ci})} \bigg|_T \quad (6-10)$$

Crystal diffusivity of the adsorbed molecules in the micropores may be explained as an activated process^{101,102} (Eq. 6-11):

$$D_{ci}^{\infty} = D_{ci0} \exp\left(\frac{-E_{ai}}{RT}\right) \quad (6-11)$$

The exponential term in this equation “expresses the probability of a molecule to having sufficient kinetic energy to surmount the energy barrier”¹⁰². D_{ci0} is the “limiting diffusivity at high temperature and E_{ai} is the activation energy”¹⁰⁴.

The average of adsorbed amount (\bar{q}_{ci}) in Equation 6 is described as^{154,157} (Eq. 6-12 and 6-13):

$$\bar{q}_{ci}(t) = \frac{3}{r_c^3} \int_0^{r_c} r^2 q_{ci}(r, t) dr \quad (6-12)$$

$$\frac{\partial q_{ci}(r, t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[D_{ci0} r^2 \frac{\partial q_{ci}}{\partial r} \right] \quad (6-13)$$

In Equation 6-6, the axial dispersion in a packed bed was calculated using a correlation developed by Wakao and Funazkri⁸⁴ (Eq. 6-14):

$$\frac{\epsilon_b D_{ax}}{D_{m,i}} = 20 + 0.5(Sc)(Re) \quad (6-14)$$

The equations that describe bed, particle and total porosity, gas density, gas viscosity, Reynolds number, Schmidt number, Sherwood number and external fluid film mass transfer

coefficient are detailed in Chapter 2 (section 2-7). The boundary and initial conditions are shown in Table 6-2.

Table 6-2: Boundary and initial conditions

Boundary conditions
$-D_{ax,i} \frac{\partial c_i}{\partial z} \Big _{z=0} = u_0 (c_{i0} - c_i _{z=0})$
$\frac{\partial c(z=L)}{\partial z} = 0$
$q_{ci}(r_C, t) = q_{ci}^* = H_i \bar{c}_{pi}$
$\frac{\partial q_{ci}}{\partial r} \Big _{(0,t)} = 0$
$\frac{\partial P}{\partial t} = 0$
Initial conditions
$q_{ci}(z, t=0) = 0$
$c_{pi}(r, 0) = 0$
$q_{ci}(r, t=0) = 0$
$c = \sum c_i = P / RT_0$

6.3.2 Numerical solution

A Linux machine running Ubuntu 16.04 with 8 processors: Intel Core i7-2600 CPU @ 3.40GHz and 16 GB of RAM were used to solve the system of equations.

The solver is written in Python 2.7 implementing a Galerkin type method to approximate solutions of integro-differential equations, symbolically. For this particular set of equations, a family of functions consisting of polynomials and signomial functions were used.

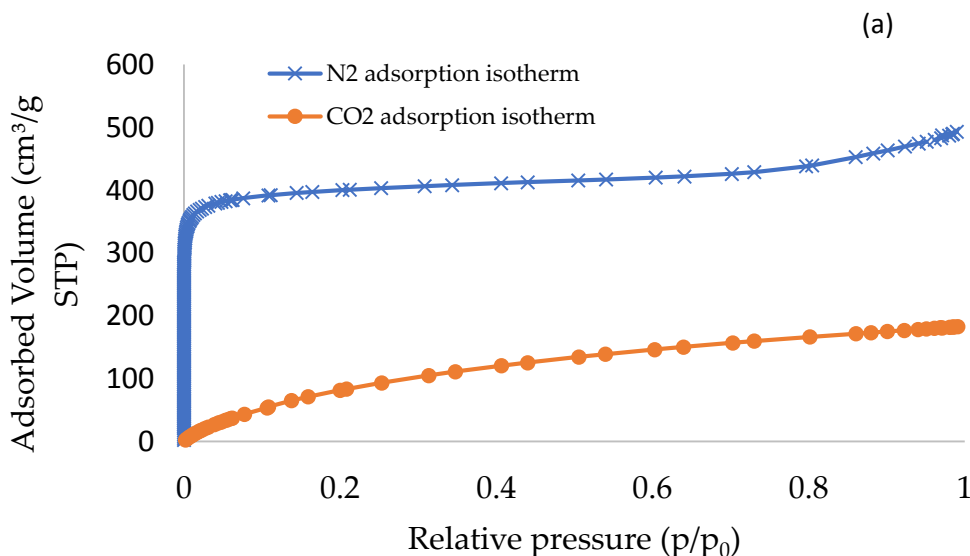
Source code: pyProximation available at <https://github.com/mghasemi/pyProximation>

6.4 Results and discussions

6.4.1 Activated carbon properties and adsorption isotherms

The characteristic properties of the activated carbon sample and the adsorption bed used in the simulations are provided in Table 6-1. N₂ adsorption-desorption isotherm at 77K, CO₂ adsorption-desorption isotherm at 273K and pore size distribution of the activated carbon are shown in Figure 6-2.

The nitrogen adsorption-desorption isotherm shows the type IV patterns of mesoporous materials. H4 hysteresis loop appeared in N₂ isotherm which is associated with the presences of narrow slit- shaped pores. The N₂ and CO₂ isotherms are similar to those reported previously^{158,159}. The pore size distribution results show a larger amount of micropore (0.48 cm³/g) resulting in a high BET specific surface area (1461 m²/g) and large particle porosity (0.549).



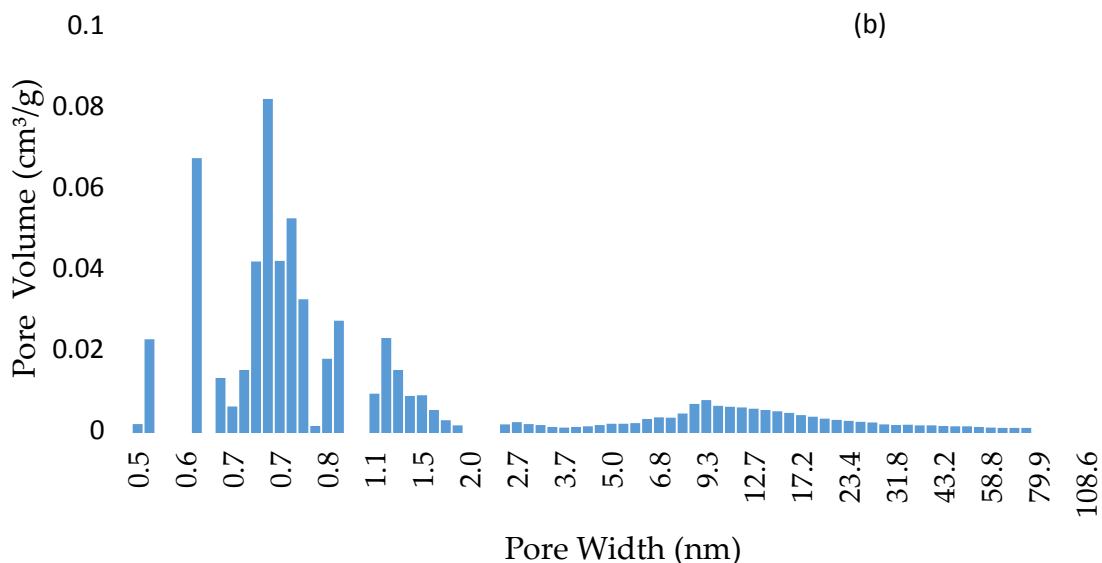


Figure 6-2: N₂ and CO₂ adsorption isotherms of activated carbon at 77 K and 273 K (a), and pore size distribution of activated carbon (b).

Figure 6- 3 shows CO₂ adsorption isotherms at 0, 25, 50 and 75 °C, respectively. The isothermal equilibrium constants (b_0), saturation capacity of CO₂ on activated carbon (q_s) and heat of adsorption of CO₂ were estimated from independent fits of CO₂ equilibrium data to Langmuir isotherm model. The fitting parameters are shown in Table 6- 3. The N₂ isotherms on activated carbon have a linear shape. The slope of the CO₂ isotherm is higher compared to that of N₂ isotherm which is associated with a better interaction of CO₂ and the activated carbon. Our previous studies also showed differential adsorption of CO₂ over N₂ on activated carbon⁵³, which confirms our assumption that competitive adsorption of N₂ is negligible. Due to exothermic nature of adsorption, CO₂ adsorption capacity decreases with increase in temperature¹⁶⁰.

Table 6-3: Fitting parameters of adsorption equilibrium and kinetic parameters for adsorption on activated carbon.

gas	q_s	b_0	$-\Delta H$	D_{ci0}/r_c^2	E_{ai}
	mol/kg	kPa ⁻¹	KJ/mol	S ⁻¹	kJ/mol
CO ₂	10.82	7.3E-6	17.44	12.995	18.05

The value of D_{ci}/r_c^2 and E_{ai} are adopted from literature while others are calculated.

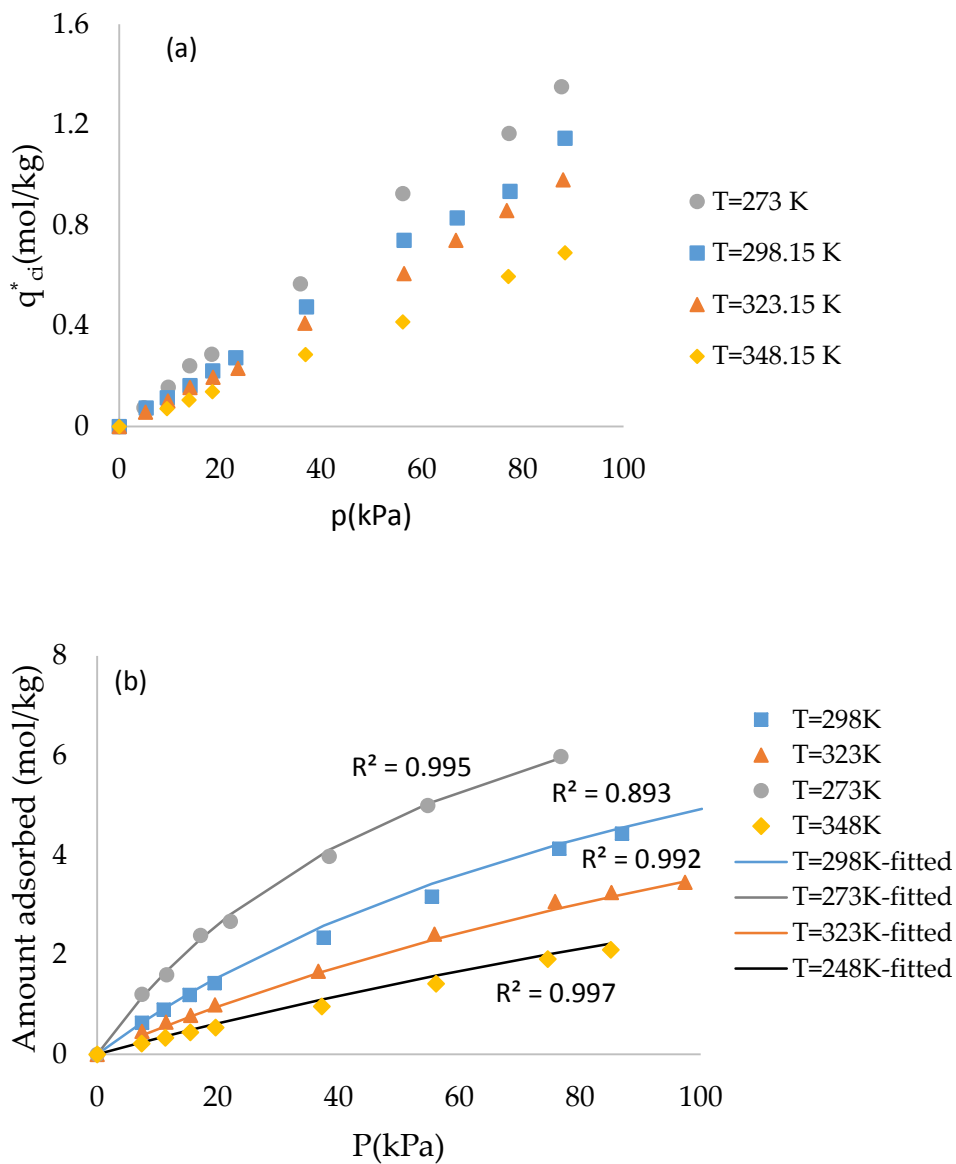


Figure 6-3: N_2 (a) and CO_2 (b) adsorption equilibrium data of activated carbon

6.4.2 Fixed-bed CO₂/N₂ mixture adsorption: experimental and modeling

A set of breakthrough CO₂ adsorption experiments with feed composition of 5-25 mol% CO₂ in N₂ at temperature range of 25-85 °C and feed flowrate of 30-70 ml/min were performed and simulated using the model described above to verify the mass transfer model and calculate the parameters at different conditions. Figures 6-4 to 6-6 show the comparison of the experimental data and simulation curves obtained for CO₂ adsorption on KOH activated carbon. In this work, the predicted gradient of C_{CO₂} at $z = L$ are compared with breakthrough experiments for CO₂ adsorption in a mixture of CO₂/N₂. Two important parameters in breakthrough curves are breakthrough point (t_b) and mass transfer zone (MTZ). Breakthrough point is a point where $C_i(z=L)/C_{i0}$ is 0.05. Most of the mass-transfer occurs in a small region when $(z=L)/C_{i0}$ varies between 0.05 to 1 which is called mass transfer zone¹⁹. The adsorption capacity of activated carbon was measured in 300 cycles and it was regenerated to more 96% of its original capacity. The adsorption capacity is reported as the number of mol of CO₂ adsorbed per kg of adsorbent (mol/kg) and it can be converted to mg/g by multiplying by 44(CO₂ molecular weight).

Figure 6-4 shows the impact of CO₂ content on adsorption of CO₂ onto activated carbon. Increase in the feed concentration results in earlier CO₂ breakthrough point and faster saturation of bed. Higher CO₂ content also results in narrower mass transfer zone and steeper breakthrough curve. Figure 6-5 shows how temperature impacts the adsorption of CO₂ onto activated carbon. Increase in temperature results in earlier breakthrough point and shorter breakthrough time which is associated with exothermic nature of adsorption process. Higher temperature also made the breakthrough curves steeper resulting in decreasing the mass transfer zone. The results indicate that the impact of temperature are more important than CO₂ content and feed flowrate. As it observed in Figure 6-6, the higher feed flowrate results in shorter retention time of the gas in the fixed bed and earlier breakthrough time and faster saturation of bed. Working at a higher feed flow rate results in more CO₂ going through bed which leads to faster saturation of bed. However, the feed flow rate doesn't have a great impact on CO₂ adsorption capacity of activated carbon. These observations are in agreement with those reported before^{160,161}.

The breakthrough CO₂ adsorption results in Figures 6-4 to 6-6 illustrate that the binary adsorption of CO₂ in N₂ on KOH activated carbon are well represented by the Langmuir model

with the parameters calculated according to single component adsorption measurements. In the case of different CO₂ initial content (see Figure 6-4), the model presents a closer prediction near breakthrough point to the experimental data as compared to data in Figures 6-5 and 6-6. The reproducibility of the experimental results with simulation confirms the assumptions in this model under this operation conditions. The experimental conditions and mass transfer parameters used in the model are summarized in Table 6-4.

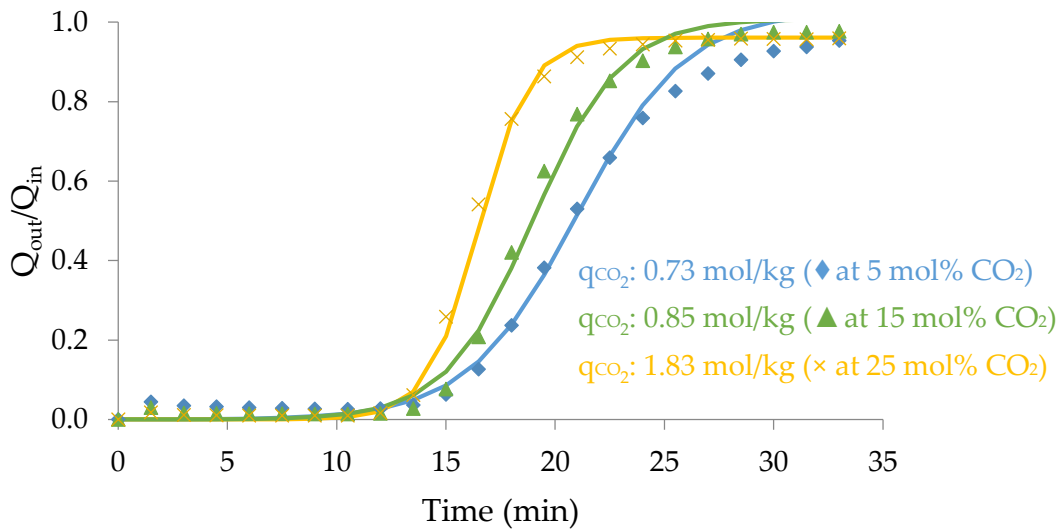


Figure 6-4: Comparison of experimentally measured breakthrough curves of CO₂ adsorption on KOH activated carbon using 5, 15 and 25 mol% CO₂ in inlet feed with model predictions. ♦, $y_{CO_2}=5$ mol%; ▲, $y_{CO_2}=15$ mol%; ×, $y_{CO_2}=25$ mol%; solid lines represent the model predictions.

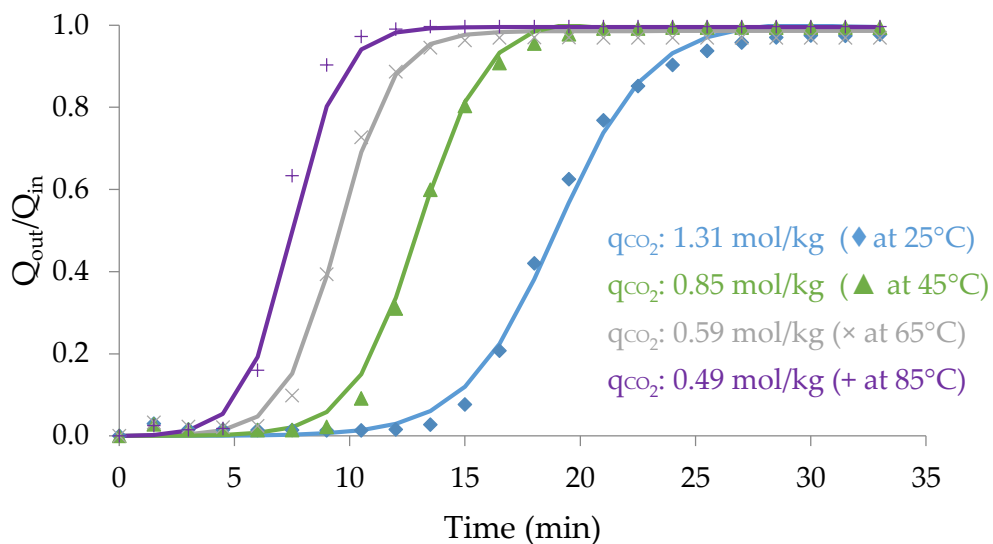


Figure 6-5: Comparison of experimentally measured breakthrough curves of CO₂ adsorption on KOH activated carbon at 25, 45, 65 and 85 °C with model predictions. ♦, T=25°C; ▲, T=45°C; ×, T=65°C; +, T=85°C; solid lines represent the model predictions.

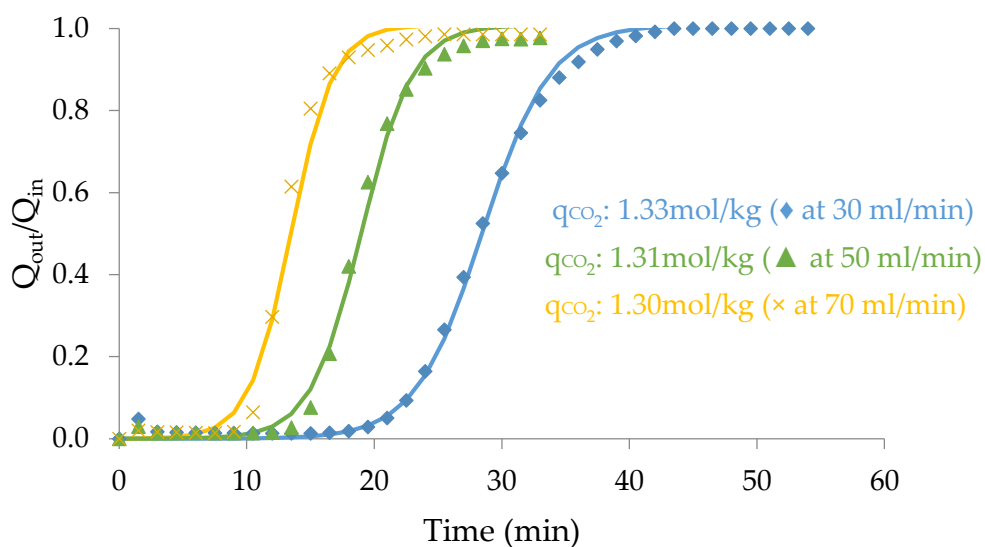


Figure 6-6: Comparison of experimentally measured breakthrough curves of CO₂ adsorption on KOH activated carbon using feed flowrate of 30, 50 and 70 ml/min with model predictions. ×, Q= 70ml/min; ▲, Q= 50ml/min; ♦, Q= 30ml/min; solid lines represent the model predictions.

Table 6-4: Experimental conditions and mass transfer parameters used in model

No.	Temperature	flowrate	mole fraction of CO ₂	D _{ax}	D _p	k _f
	°C	ml/min	Mol%	cm ² /s	cm ² /s	cm/s
1	25	50	15	2.724	2.962×10 ⁻³	7.488
2	45	50	15	3.051	3.0693×10 ⁻³	8.329
3	65	50	15	3.394	3.173×10 ⁻³	9.210
4	85	50	15	3.752	3.273×10 ⁻³	10.130

6.4.3 Controlling mass transfer step

According to Silva ¹⁶², the controlling mechanism in adsorption process can be disguised using Equations 6-15 and 6-16. If $\gamma (1 + \alpha) < 0.1$, then the micropore diffusion is the controlling mechanism in adsorption process; if $\gamma (1 + \alpha) > 10$, then the macropore diffusion is the controlling mechanism in adsorption process and if $0.1 < \gamma (1 + \alpha) < 10$ then both macropore and micropore diffusion are important in the adsorption process,

$$\gamma = \frac{D_c/r_c^2}{D_p/R_p^2} \quad (6-15)$$

$$\alpha = \frac{1 - \varepsilon_p}{\varepsilon_p} H \quad (6-16)$$

According to the calculated parameters in this system, $\gamma (1 + \alpha) < 0.1$, which confirms that the micropore resistance is the controlling mass transport mechanism for CO₂ adsorption on KOH activated carbon under the studied adsorption condition. These results confirm that the microspores play a critical role in CO₂ adsorption at post combustion flue gas conditions.

6.5 Conclusions

The fixed-bed adsorption of CO₂ from CO₂/N₂ mixtures on activated carbon was studied. The single-component adsorption equilibrium of CO₂ and N₂ were measured at 0, 25, 50 and 75 °C

and fitted with the Langmuir model. An isothermal bi-LDF model was developed for CO₂ adsorption in a binary mixture of CO₂/N₂. The breakthrough curves of the CO₂ adsorption from CO₂/N₂ mixtures on activated carbon were measured experimentally and compared to theoretical breakthrough curves at different experimental conditions such as feed flow rate, adsorption temperature, and feed concentration. Higher feed flowrate and higher CO₂ content result in earlier breakthrough time, however temperature has the greatest impact on CO₂ adsorption on activated carbon. It was observed that the decrease in temperature results in a longer breakthrough time and wider mass transfer zone. According to the experimental data and simulation results, it was confirmed that the micropore diffusion is the controlling step for CO₂ adsorption on the microporous activated carbon.

Chapter 7 Conclusions and Recommendations for Future Work

7.1 Conclusions

The overall objective of this work was to (1) understand the impact of precursors, pyrolysis conditions and activating agents on physical properties and adsorption performance of activated carbon, (2) understand the effect of process conditions on the adsorption process and optimize these conditions, (3) enhance CO₂ adsorption performance of the activated carbon using metal impregnation, and (4) develop a mass transfer model to simulate and predict CO₂ adsorption for scale-up of this process.

This study examined the effects of three different types of activating agents on physical and chemical properties of the activated carbon. The adsorption performance of the prepared activated carbons was then tested under a temperature range of 25–65°C and inlet CO₂ concentration range of 10–30 mol.% in inert gas. Decrease in temperature and increase in initial CO₂ content resulted in higher CO₂ adsorption. KOH activated carbon with larger surface area and microporous structure had a better performance for CO₂ adsorption. However, at high temperature and/or low concentration of CO₂, all activated carbon samples show poor CO₂ adsorption capacities. The optimum conditions for better CO₂ are low temperature and high CO₂ content.

Study of the impact of biomass and pyrolysis method revealed that the significant differences in surface chemistry, porous structure and morphology of the activated carbons are resulted from pyrolysis conditions. Overall for the same precursor, the fast pyrolysis process led to larger surface area and total pore volume, smaller particle size and ultra-pore volume, and a larger contribution of phenolic/ketone and carboxylic groups. However, activating agent determined the porosity of the activated carbon and impact of the pyrolysis method and biomass is not as remarkable as that of activating agent.

The CO₂ uptake is closely related to the pore size distribution of activated carbons the gas diffusion in activated carbons is controlled within the micropore resistance¹⁵³. The enlargement of the pore width of microspores resulted in remarkable decrease in CO₂ adsorption capacity. Similar behavior was reported before for AC at different tempearture^{55,136,153}. This result is a key

point of this thesis and optimization of pyrolysis/activation process to maximize the ration of the ultra-micropore volume to total pore volume for better CO₂ adsorption capacity and selectivity required attention.

To improve CO₂ adsorption at moderate temperature, MgO impregnated activated carbon was prepared using different preparation methods. Preparation method affects the porosity and metal dispersion on activated carbons. Impregnation of activated carbon with magnesium oxide improved the adsorption performance by increasing the breakthrough time. However, increase in breakthrough time is more remarkable at higher temperature. Comparison of the results of CO₂ adsorption on MgO-impregnated activated carbon at 100 °C with not-impregnated activated carbon shows a 65% increase using MgO impregnated activated carbon.

An isothermal bi-LDF model was developed to simulate the CO₂ adsorption experiments. The equilibrium data were fitted to Langmuir isotherm and the developed model was compared to experimental results. It was confirmed that the controlling mass transfer step is micropore mass transfer resistance.

7.2 Recommendations for future work

- Impact of presence of moisture and other greenhouse gases such as moisture, methane, carbon monoxide, SO₂ and NO_x on adsorption capacity and selectivity of activated carbon should be studied.
- Different methods of gas desorption such as vacuum desorption or combination of thermal and vacuum desorption should be tested to optimize the desorption process.
- Feasibility study and life cycle assessments of the fixed-bed adsorption and technical-economical comparison of this technology should be performed with the existing absorption units to evaluate the industrial application of this process.
- A comparison of the promising solid sorbents such as zeolite, MOFs and carbo nanotubes based on technical and economical evaluation should be studied.
- Surface chemistry and micro-structure of saw dust from different sources as a precursor of activated carbon should be evaluated.

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Appendix A : Steam, CO₂ and KOH activation set-up for production of activated carbons

Activation of biochar with steam:

The schematic of steam activation set-up for is shown in Figure A.1. A fixed bed, Inconel reactor (25.4 mm OD, 22 mm ID, length of 870 mm) was used for activation of biochar with steam. A vertical furnace (3210 series, max temperature of 1200 °C, Applied Test System Inc.) was used to keep the reactor at a constant temperature. Temperature calibration of bed was recorded by placing a K-type thermocouple in the middle of the bed and is shown in Figure A.2.

Temperatures of the furnace and boiler were controlled by two temperature controllers (Eurotherm 2416 and Omega CN 7500, respectively). Nitrogen flow was controlled by a mass flow controller (Brooks Instrument, 5850S) and the calibration data is shown in Figure A.3. Water is injected by a metering pump (Genie Kent) to the boiler and steam was generated in a boiler (stainless steel tube embedded in a insulated aluminum block). The calibration data of water injection pump is shown in Figure A.4.

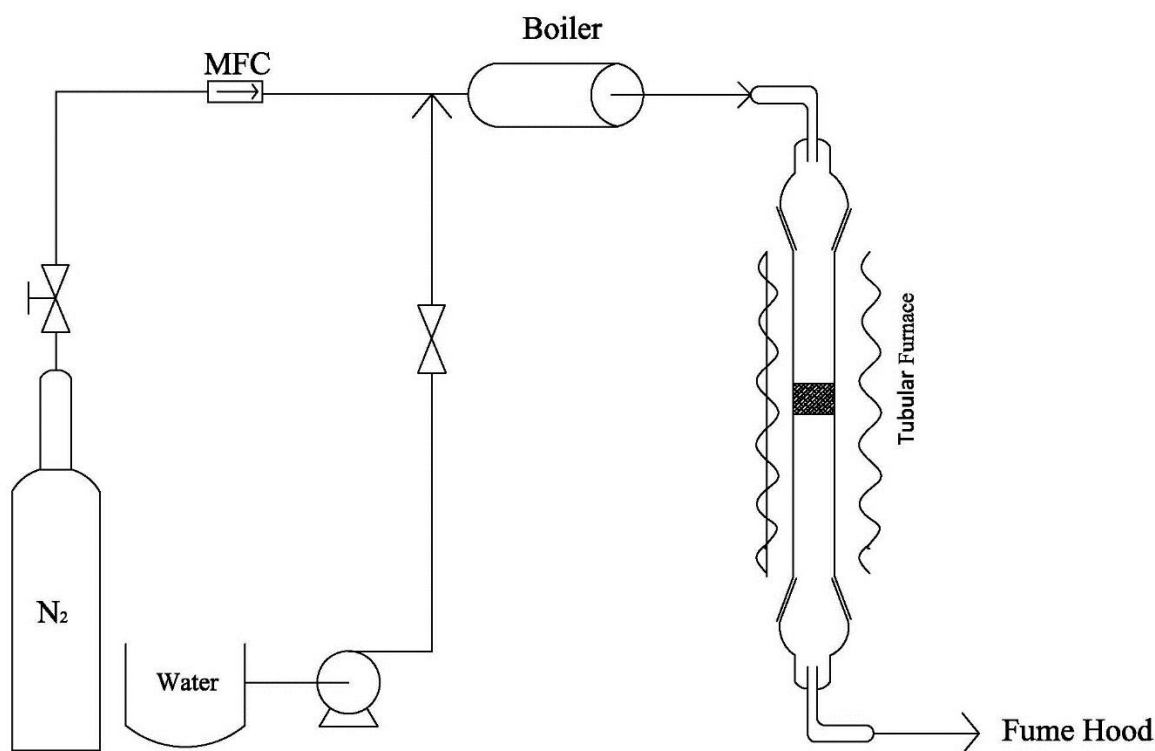


Figure A.1: Schematic of steam activation set-up

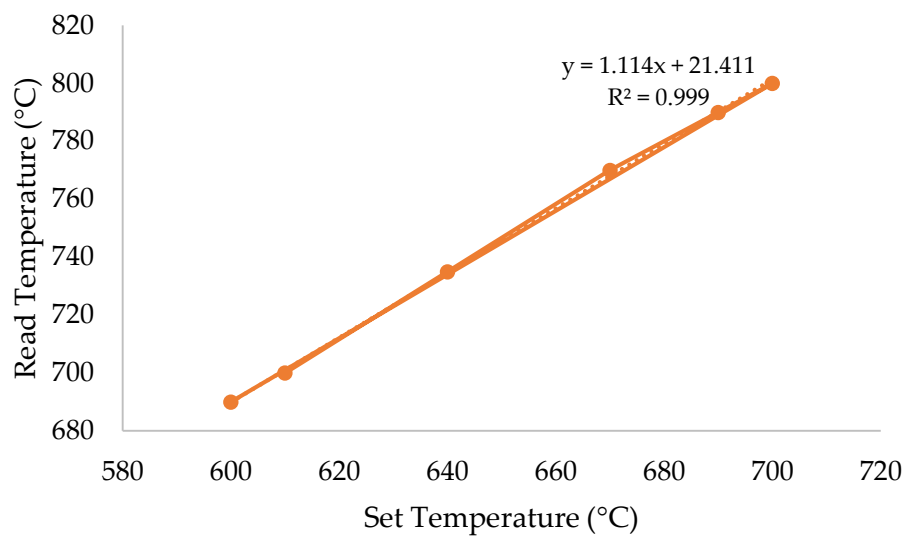


Figure A.2: Temperature calibration data for the furnace installed on the steam activation set-up

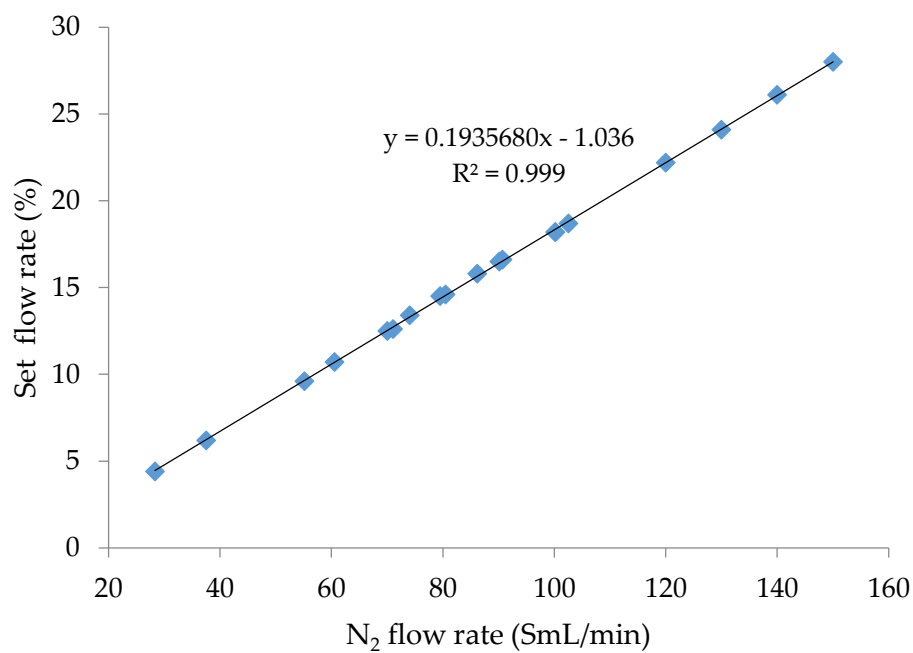


Figure A.3: Calibration data for N₂ mass flow controller used in the steam activation set-up

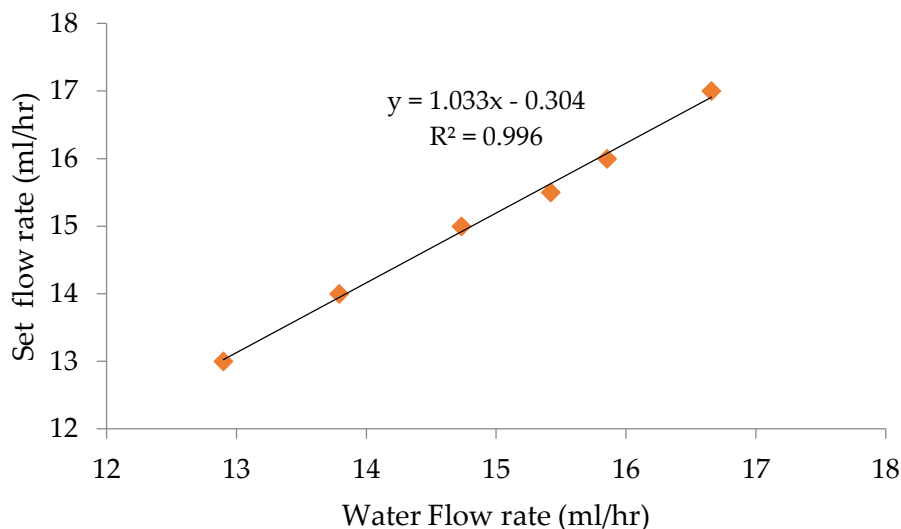


Figure A.4: Calibration data for water injection pump used for steam generation

Activation of biochar with CO₂:

The schematic of experimental set-up for biochar activation with CO₂ is shown in Figure A.5. A fixed bed, Inconel reactor (25.4 mm OD, 22 mm ID, length of 660 mm) was used for activation of biochar with CO₂. A vertical furnace (3210 series, max temperature of 1200 °C, Applied Test System Inc.) was used to keep the reactor at a constant temperature. Temperature of the furnace was controlled by a temperature controller (Eurotherm 2416) and temperature calibration data of bed is shown in Figure A.6. Argon and CO₂ flow were controlled by a mass flow controller (Brooks Instrument, 5850S A/B) and the calibration data is shown in Figures A.7 and A.8, respectively.

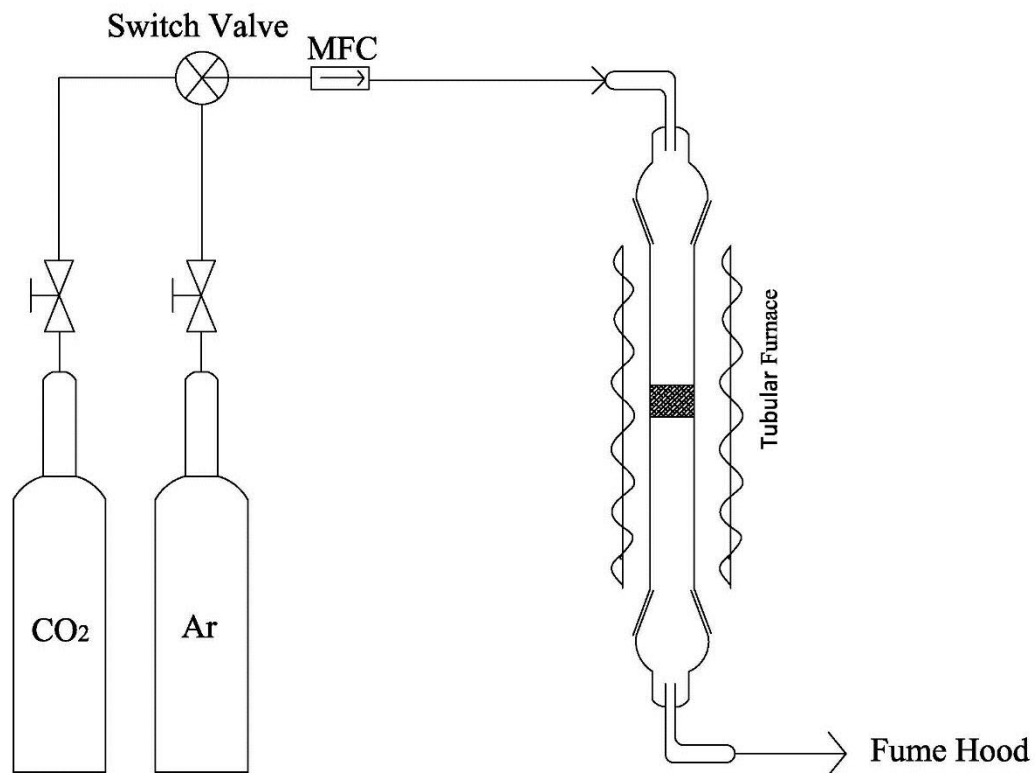


Figure A.5: Schematic of CO₂ activation set-up

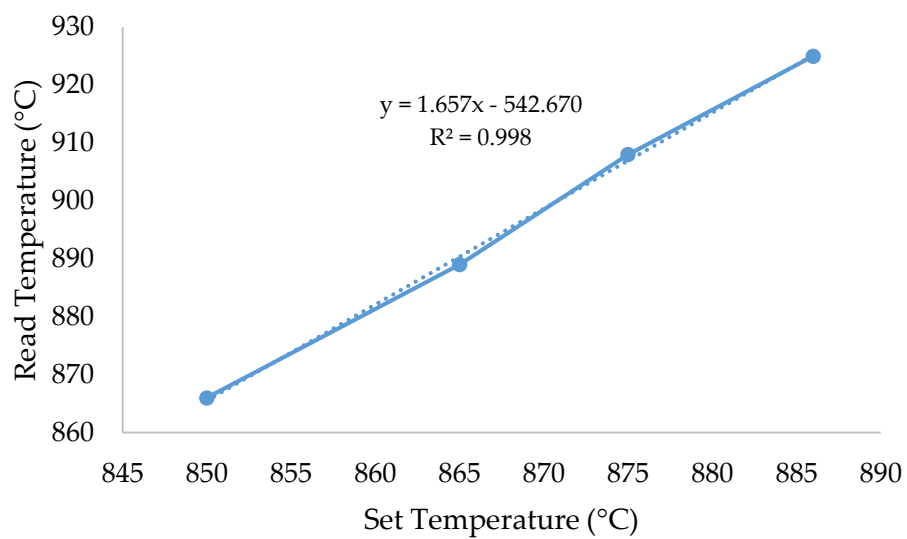


Figure A.6: Temperature calibration data for the furnace installed on the CO₂ activation set-up

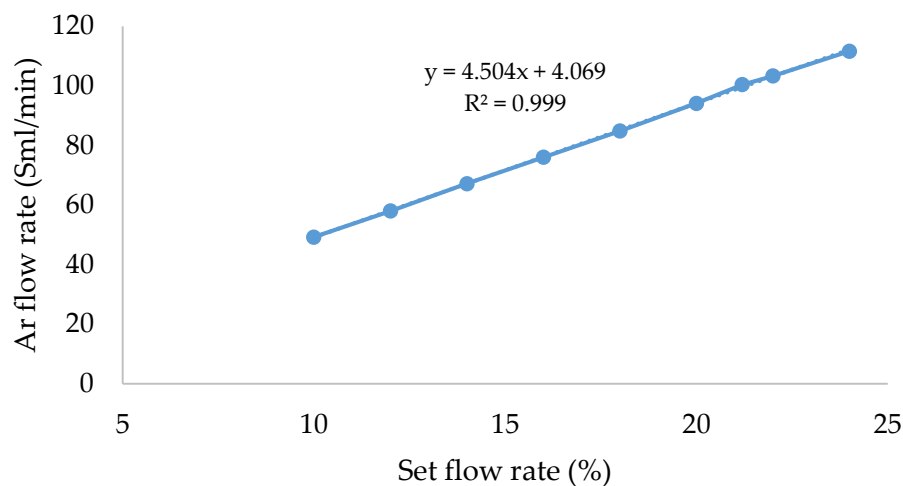


Figure A.7: Calibration data for Ar mass flow controller used in the CO₂ activation set-up (at 100 psi)

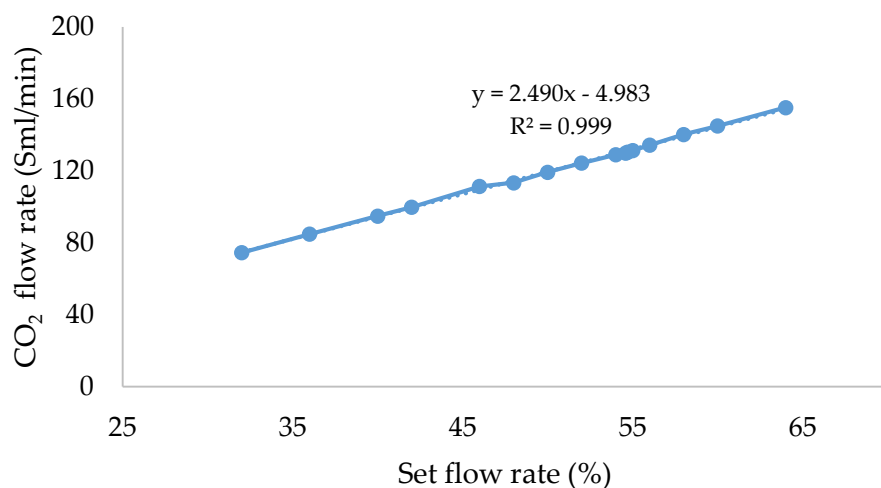


Figure A.8: Calibration data for CO₂ mass flow controller used in the CO₂ activation set-up (at 150 psi)

Activation of biochar with KOH:

KOH activation of biochar was carried out in the experimental set-up that was used for steam activation process (water injection line was blocked). Calibration data in Figure A.2 and A.3 are also valid for KOH activation.

Appendix B : Fixed reactor specifications and calibration curves for CO₂ adsorption experiment in chapter 3

A fixed-bed reactor set-up for CO₂ adsorption experiments was designed and built at the Department of Chemical and Biological Engineering, University of Saskatchewan. An Inconel tubular reactor was used for CO₂ adsorption experiments. A heating tape (Silicone rubber insulated heating tape, Cole-Parmer) was used to supply heat to the reactor. It could be operated to a maximum temperature of 232 °C. Bed temperature was controlled by placing a K-type thermocouple in the middle of the bed coupled with a temperature controller (Eurotherm-2416). Specification of the fixed-bed reactor is shown in Table B.1. The flow rate of CO₂ and He were controlled by a mass flow controllers (Brooks Instrument, 5850S, max flow 200 ml/min) and a metering valve coupled with a mass flow meter (Brooks Instrument, 5860S, max flow 500 ml/min). Calibration data for CO₂ and He are given in Figures B.1 and B.2.

Table B.1: Specifications of fixed-bed reactor

bed diameter	cm	2.5
bed height	cm	6
column length	cm	42

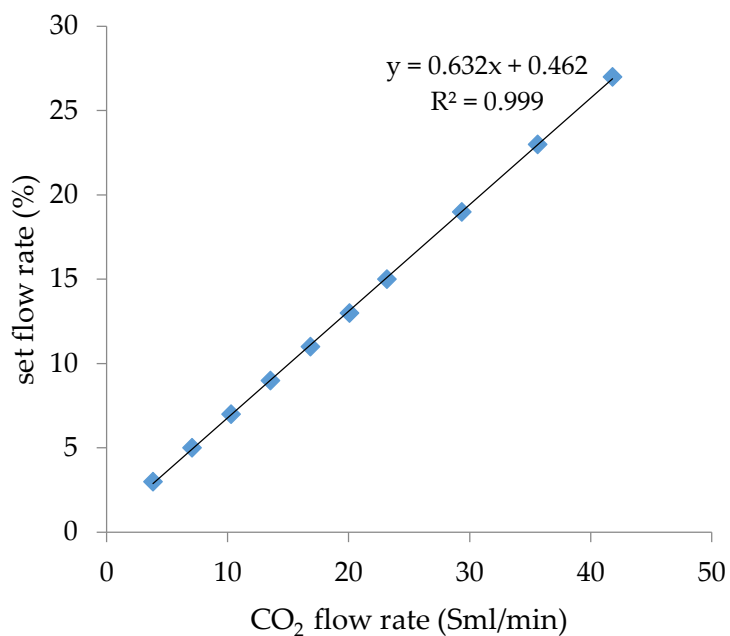


Figure B.1: Calibration data for CO₂ mass flow controller used in the CO₂/He adsorption experiment at 100 psi

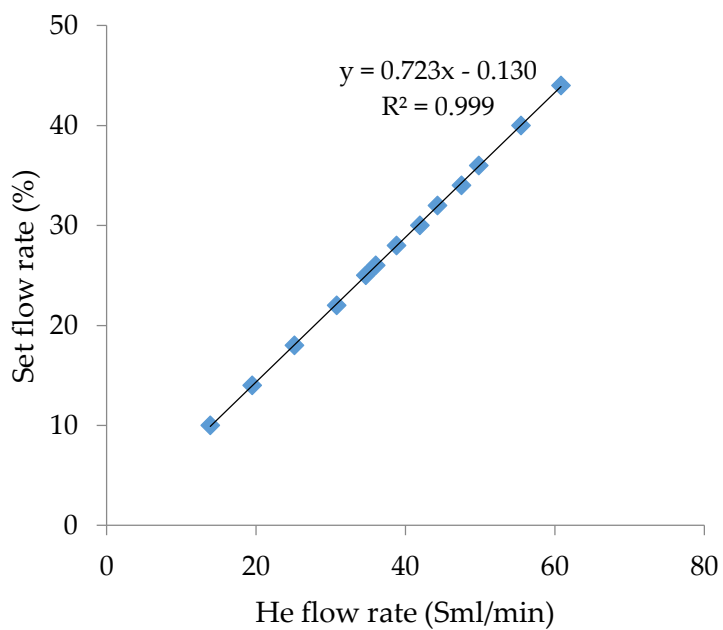


Figure B.2: Calibration data for He mass flow controller used in the CO₂/He adsorption experiment at 100 psi

GC Calibration Table

GC calibration date on Sep 5, 2013 is shown in Table B.2 and Table B.3.

Table B.2: GC Calibration data used in chapter 3

RetTime [min]	Lvl Sig	Amount [%]	Area	Amt/Area	Ref Grp Name
0.331	3 1	4.99000	72.19977	6.91138e-2	Helium
0.361	3 1	9.97000	236.94647	4.20770e-2	H2
0.405	4 1	7.01000	29.96327	2.33953e-1	CO2
0.428	4 1	3.00000	13.14342	2.28251e-1	Ethylene
0.447	4 1	4.98000e-1	2.31539	2.15082e-1	Ethane
0.477	4 1	4.98000e-1	1.60827	3.09649e-1	Acetylene
0.481	3 1	2.00000	5.55207	3.60226e-1	O2
	2	20.78000	50.79090	4.09128e-1	
0.636	3 1	62.32300	136.96855	4.55017e-1	N2
	2	74.19000	156.21611	4.74919e-1	
0.748	4 1	7.01000e-1	3.82498	1.83269e-1	Propane/Propylene
0.897	3 1	5.99000	35.67048	1.67926e-1	Methane
1.364	3 1	8.01000	17.34495	4.61806e-1	CO

Table B.3: Composition of standard gas used for GC calibration

Component	Certified Concentration	Analytical Accuracy
acetylene	0.498	±2%
Propane	0.200	±2%
Propylene	0.501	±2%
Ethane	0.498	±2%
Ethylene	3.00	±2%
Methane	5.99	±2%
Carbon monoxide	8.01	±2%
Hydrogen	9.97	±2%
Carbon dioxide	7.01	±2%
Oxygen	2.00	±2%
Nitrogen	62.32	±2%
Praxair Part Number:	NI AC5000X3C-AS	

Appendix C : The ANOVA results of CO₂ activated carbon

The experimental results of CO₂ adsorption on CO₂ activated carbon are fitted with a quadratic model that proved best for lack of fit and model statistics tests. Table C.1 presents ANOVA of CO₂ adsorption model on CO₂ activated carbon. Although the Predicted R² of 0.93 is in reasonable agreement with the Adj-R² of 0.98(the difference < 0.2), there is significant lack of fit (0.0004) which indicates that the provisional model is inadequate.

Table C.1: The ANOVA results of the response surface quadratic model of CO₂ activated carbon

	Sum of square	Mean square	df	p-value
Model	2624.98	656.25	4	<0.0001
T	1009.91	1009.91	1	<0.0001
C _{CO₂}	1498.70	1498.70	1	<0.0001
T. C _{CO₂}	82.25	82.27	1	0.0041
C _{CO₂} . C _{CO₂}	34.11	34.11	1	0.0335
residual	41.54	5.20	8	
Lack of fit	41.05	10.26	4	0.0004
Pure error	0.49	0.12	4	0.0041
Total	2694.23		13	
Std. Dev.	2.43			
R ²	0.99			
Adj-R ²	0.98			
Predicted R ²	0.93			

Appendix D : Willow ring characteristic, GC calibration data, fixed-bed reactor specifications and related calibrations for CO₂ adsorption experiment in chapter 4

Physical characteristics of willow ring (biomass) is shown in Table D.1.

Table D.1: Approximate analysis of willow ring

Moisture Content	8.4 wt.%
Ash content	1.9 wt.%
Volatile matter	79.3 wt.%
Fixed carbon*	10.4 wt.%

*Fixed carbon is calculated by difference

The temperature calibration data used for slow pyrolysis of biomass sample in chapter 4 is provided in Figure D.1.

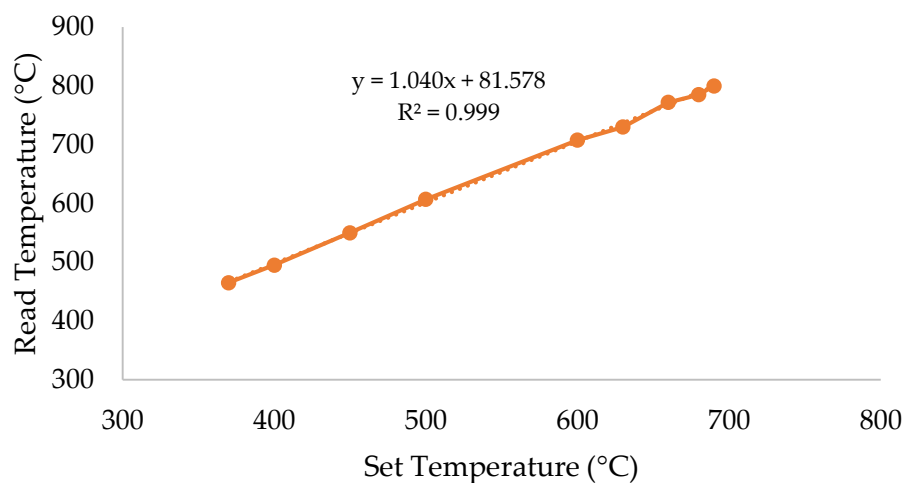


Figure D.1: Temperature calibration data for the furnace used for slow pyrolysis

GC Calibration Table

GC calibration data used in chapter 4 is shown in Table D.2

Table D.2: GC calibration Data on 21 March, 2014

RetTime [min]	Lvl Sig	Amount [%]	Area	Amt/Area	Ref Grp Name
0.329	3 1	4.99000	72.19977	6.91138e-2	Helium
0.364	3 1	9.97000	236.94647	4.20770e-2	H2
0.402	4 1	7.01000	29.96327	2.33953e-1	CO2
	4	20.00000	90.77847	2.20317e-1	
0.429	4 1	3.00000	13.14342	2.28251e-1	Ethylene
0.446	4 1	4.98000e-1	2.31539	2.15082e-1	Ethane
0.477	4 1	4.98000e-1	1.60827	3.09649e-1	Acetylene
0.481	3 1	2.00000	5.55207	3.60226e-1	O2
	2	20.78000	50.79090	4.09128e-1	
0.650	3 1	62.32300	136.96855	4.55017e-1	N2
	2	74.19000	156.21611	4.74919e-1	
	3	100.00000	210.75797	4.74478e-1	
0.748	4 1	7.01000e-1	3.82498	1.83269e-1	Propane/Propylene
0.897	3 1	5.99000	35.67048	1.67926e-1	Methane
1.364	3 1	8.01000	17.34495	4.61806e-1	CO

Specification of the fixed-bed reactor is shown in Table D.3. The flow rate of CO₂, O₂ and N₂ were controlled by three mass flow controllers of Brooks Instrument 5850E and max flow of 200ml/min, Brooks Instrument 5850TR and max flow of 12SLPH, and Brooks Instrument 5850S and max flow of 200ml/min, respectively. Calibration data for CO₂, O₂ and N₂ mass flow controllers are given in Figures D.2, D.3 and D.4.

Table D.3: Specifications of the fixed-bed reactor used in chapter 4

reactor material	stainless steel	
bed diameter	cm	2.5
bed height	cm	5
column length	cm	42

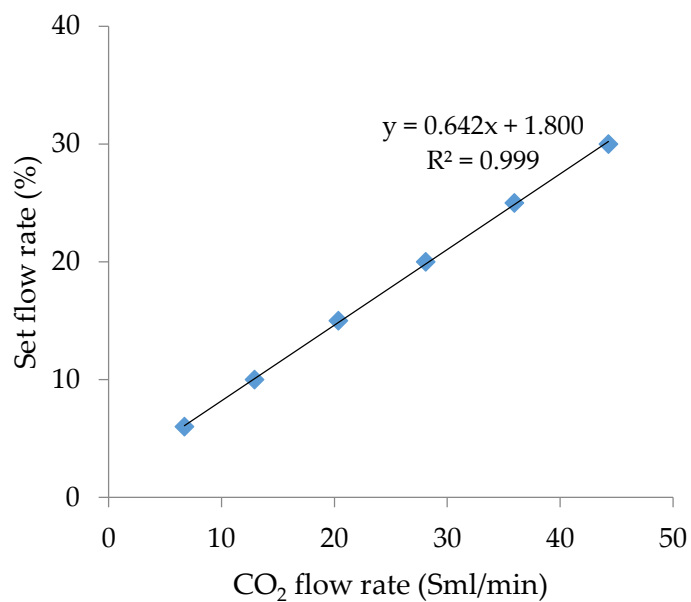


Figure D.2: Calibration data for CO₂ mass flow controller used in the CO₂/O₂/N₂ adsorption experiment at 100 psi

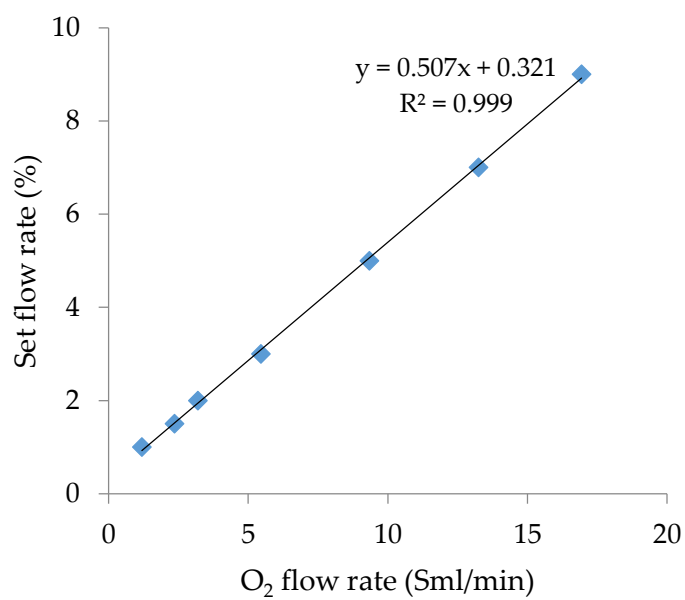


Figure D.3: Calibration data for O₂ mass flow controller used in the CO₂/O₂/N₂ adsorption experiment at 100 psi

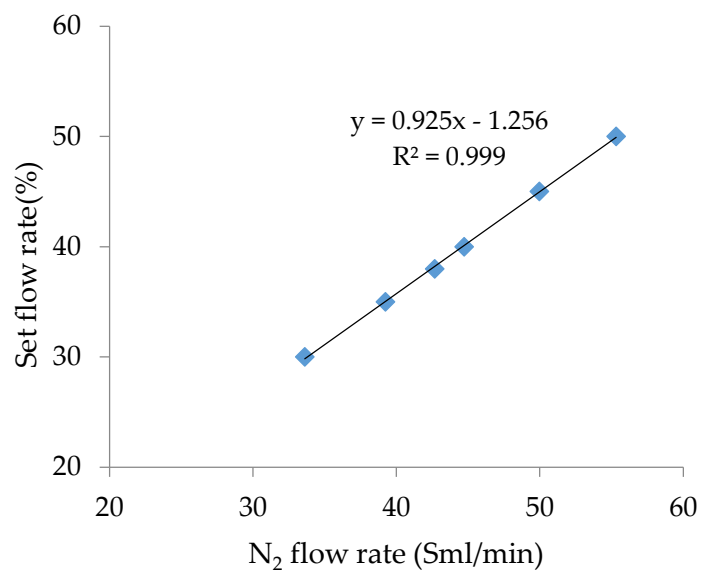


Figure D.4: Calibration data for N₂ mass flow controller used in the CO₂/O₂/N₂ adsorption experiment at 100 psi

Appendix E : Calibration data and calculations used in Chapter 5

Temperature calibration data of the tubular furnace installed on the calcination set-up is shown in Figure E.1. Calibration data used for injection pump used for steam generation is shown in Figure E.2

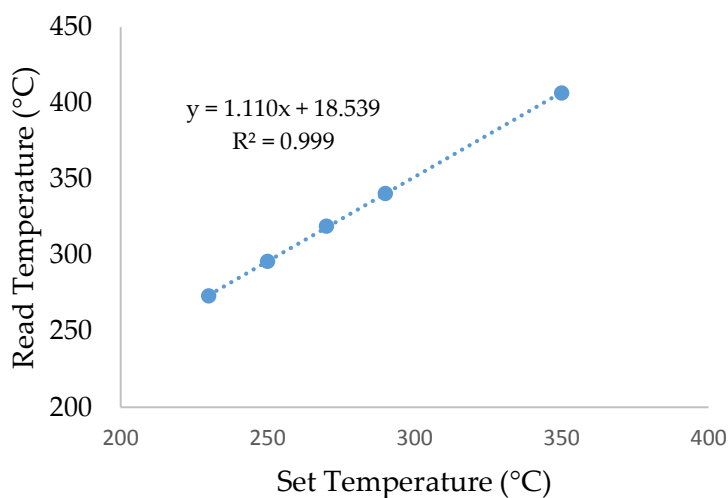


Figure E.1: Temperature calibration curve of the furnace installed on the calcination set-up

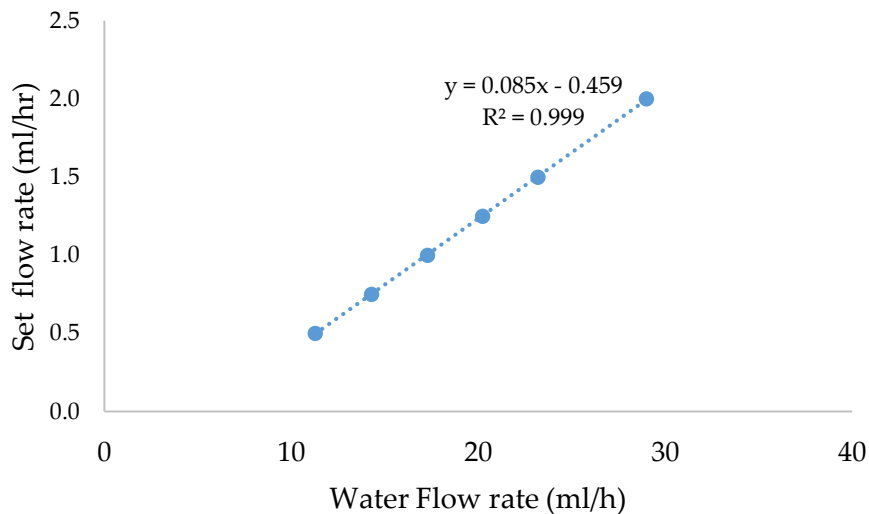


Figure E.2: Calibration data for water injection pump used for steam generation in Chapter 5

1- Excess Solution Impregnation of Biochar

To produce 3 and 10 wt. % MgO impregnated activated carbons, the biochar was treated with magnesium nitrate in 100 ml water for 15 h at room temperature. Then the sample was dried at 100 °C for 15 h in an oven followed by the steam activation process. The yield of activation process is ~51% and the initial salt content in the bath was selected in order to have 3 and 10 wt. % Mg in the final product. The metal content after rinsing was calculated based on the weight loss after rinsing. Details of preparation of excess solution impregnation of biochar are shown in Table E.1.

Table E.1: Preparation details of excess solution impregnation of biochar

Sampl es	Bioch ar weigh t (g)	Mg(NO ₃) ₂ .6H ₂ O (g)	Wat er (ml)	after activati on weight (g)	Activation Temperatu re (°C)	carbo n weig ht (g)	weight differen ce (g)	metal conte nt (g)	metal conte nt (%)
3MgO -B	24.25	4.34	100. 0	13.05	700	12.37	0.68	0.41	3.2%
3MgO -B-R	24.25	4.34	100. 0	12.78	700	12.37	0.41	0.25	1.9%
10Mg O-B	22.50	15.39	100. 0	13.89	700	11.48	2.42	1.46	10.5 %
10Mg O-B-R	22.50	15.39	100. 0	13.05	700	11.48	1.58	0.95	7.3%

2- Excess Solution and Incipient Wetness Impregnation of Activated Carbon

For excess solution impregnation, steam activated carbons were impregnated in 100 ml water with metal nitrate of an appropriate concentration for 15 h to produce 3 and 10 wt. % of metal in

the final product. The mixtures of AC and solutions of metal nitrate were then dried in the oven for 15 h. The procedure was followed by calcination at 325 °C for 4 h. The metal content of the rinsed samples was calculated based on the weight loss after rinsing.

For incipient wetness impregnation, steam activated carbon was impregnated with Mg salt solution drop by drop. The mixture was kept at room temperature for 15 h. Then the sample was dried at 100 °C for 15 h in an oven followed by calcination at 325°C for 4h. Table E.2 shows the details of excess solution preparation and incipient wetness impregnation of activated carbon.

Table E.2: preparation details of excess solution and incipient wetness impregnation of activated carbon

Samples	after activation weight (g)	Mg(NO ₃) ₂ .6 H ₂ O (g)	Water (ml)	Impregnated Activated Carbon (g)	Weight difference (g)	Metal content (g)	Metal content (%)	Calcination temperature (°C)
3MgO-AC	9.70	3.16	100.0	10.20	0.50	0.30	3.0%	325
3MgO-AC-R	9.70	3.16	100.0	9.94	0.24	0.14	1.5%	325
3Mgo-AC- DRY	9.70	3.16	2.6	10.23	0.53	0.32	3.1%	325
10MgO-AC	9.00	10.55	100.0	10.76	1.76	1.06	9.9%	325
10MgO-AC- R	9.00	10.55	100.0	10.32	1.32	0.80	7.7%	325
10Mgo-AC- DRY	9.00	10.55	2.4	10.78	1.78	1.07	10.0%	325

Appendix F : Calibration data and calculations used in Chapter 6

Skeletal Density Calculations:

The gas pycnometer (ultra-pycnometer 1000, Quantachrome Instruments) determines the skeletal density of activated carbon powders based on Eq. F-1 assuming an ideal gas:

$$V_p = V_c + V_R \left[\frac{P_1}{P_2} - 1 \right] \quad (\text{F-1})$$

where

V_p : the sample volume

V_c : the volume of the empty sample chamber (known from a prior calibration step)

V_a : the volume of the reference volume (again known from a prior calibration step)

P_1 : the first pressure (i.e. in the sample chamber only)

P_2 : the second (lower) pressure after expansion of the gas into the combined volumes of sample chamber and the reference chamber

Helium is used as the displacing fluid in pycnometer since it penetrates the finest pores approaching one Angstrom. Sample calculation is shown below in Table F.1.

Table F.1: Sample calculation on skeletal density

Weight of activated carbon powders	18.910	g
P_1	16.609	
P_2	6.560	
V_a	90.529	cm ³

V_c	147.634	cm^3
V_p	8.956	cm^3
Skeletal Density	2.111	g/cm^3

Temperature Calibration Data of Furnace Installed on Steam Activation Setup

Figure F.1 shows the temperature calibration data of the furnace installed on activation set-up.

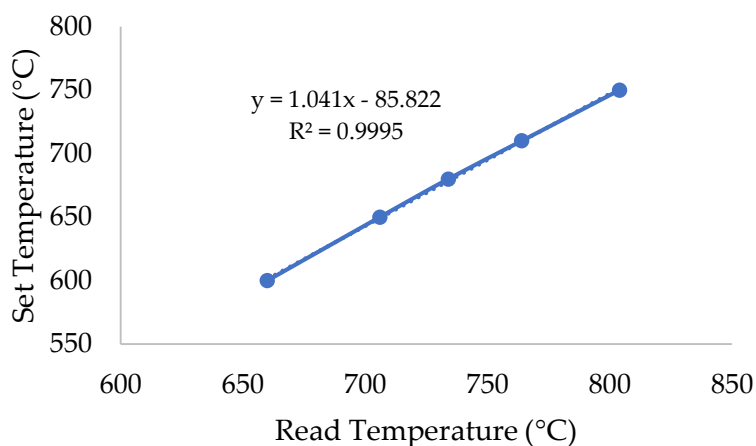


Figure F.1: Temperature calibration data for the furnace installed on the steam activation set-up used in Chapter 6

Adsorption isotherms of CO_2 and N_2 are fitted to dual site Langmuir isotherms using CO_2/Ar and N_2/Ar gas mixture at different temperatures. The flow rate of CO_2 , Ar and N_2 were controlled by three mass flow controllers of Brooks Instrument 5850E and max flow of 200 ml/min, Brooks Instrument 5850S and max flow of 200ml/min, and Brooks Instrument 5850TR and max flow of 12SLPH, respectively. Calibration data for CO_2 , O_2 and N_2 mass flow controllers are given in Figures F-2, F-3 and F-4.

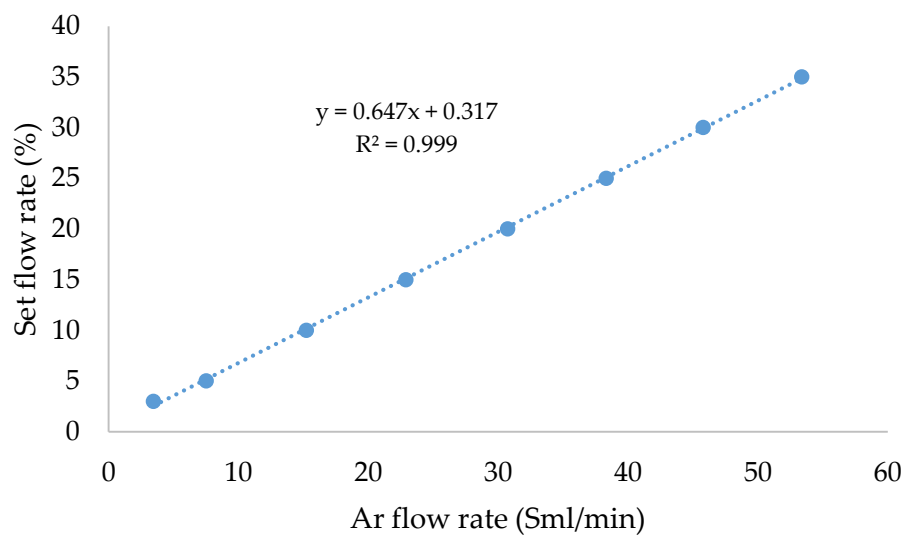


Figure F.2: Calibration data for N₂ mass flow controller used in the Ar/N₂ and Ar/CO₂ adsorption experiments (N₂ and CO₂ adsorption isotherms) at 100 psi

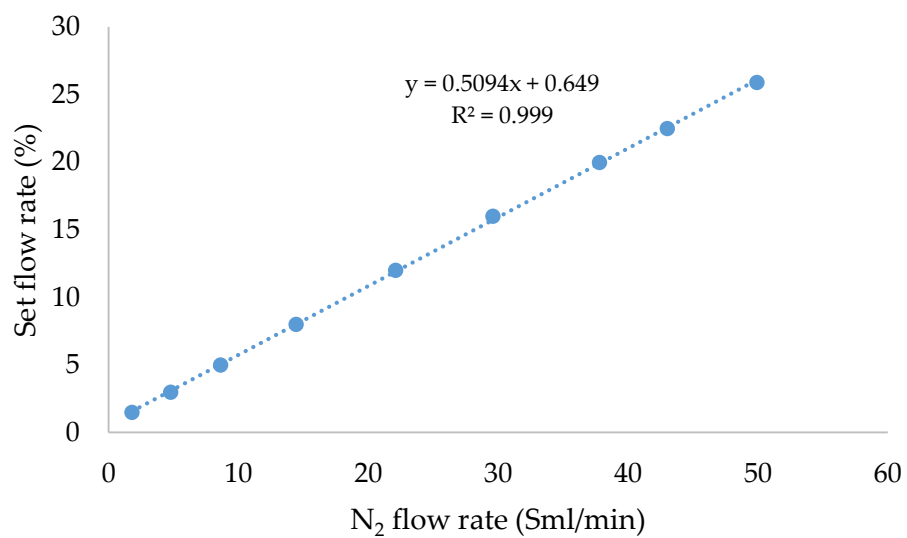


Figure F.3: Calibration data for N₂ mass flow controller used in the Ar/N₂ adsorption experiments (N₂ adsorption isotherms) at 100 psi

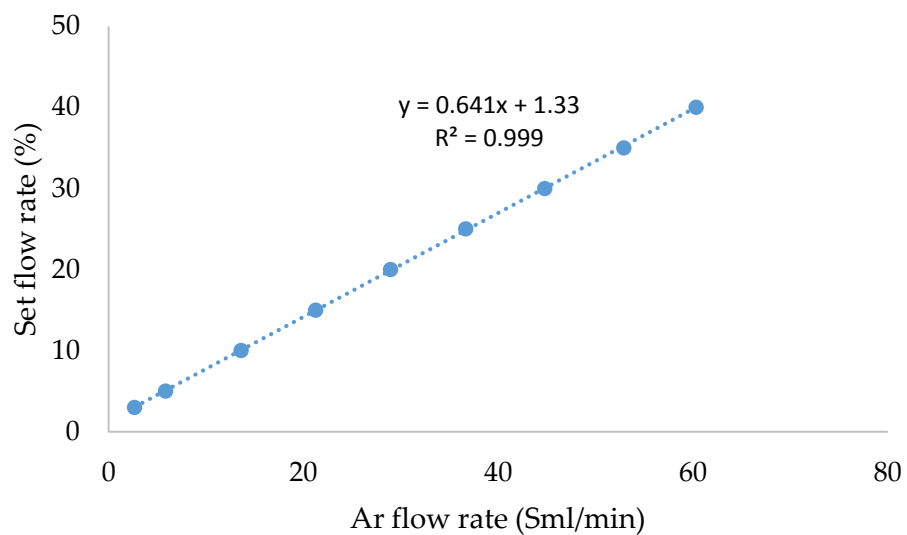


Figure F.4: Calibration data for N₂ mass flow controller used in the Ar/CO₂ adsorption experiments (CO₂ adsorption isotherms) at 100 psi

GC Calibration Table

GC Calibration Date on February 17, 2016 is shown in Table F.2

Table F.2: GC calibration data on February 17, 2016



RetTime	Lvl	Amount	Area	Amt/Area	Ref Grp Name
[min]	Sig	[%]			
0.348	3 1	4.99000	72.19977	6.91138e-2	Helium
0.364	3 1	9.97000	236.94647	4.20770e-2	H2
0.410	4 1	7.01000	29.96327	2.33953e-1	CO2
	4	20.00000	90.77847	2.20317e-1	
0.432	4 1	3.00000	13.14342	2.28251e-1	Ethylene
0.451	4 1	4.98000e-1	2.31539	2.15082e-1	Ethane
0.459	3 1	2.00000	5.55207	3.60226e-1	O2
	2	20.78000	50.79090	4.09128e-1	
0.483	4 1	4.98000e-1	1.60827	3.09649e-1	Acetylene
0.582	3 5	9.50000	18.59585	5.10867e-1	N2
	1	62.32300	136.96855	4.55017e-1	
	2	74.19000	156.21611	4.74919e-1	
	3	100.00000	210.75797	4.74478e-1	
0.748	4 1	7.01000e-1	3.82498	1.83269e-1	Propane/Propylene
0.897	3 1	5.99000	35.67048	1.67926e-1	Methane
1.364	3 1	8.01000	17.34495	4.61806e-1	CO

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Publication: Energy & Fuels

Publisher: American Chemical Society

Date: Nov 1, 2015

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Publication: Industrial & Engineering Chemistry Research

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